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THE ACTION OF PYRIDINE ON D-MANNITOL HEXANITRATE¹

BY J. R. BROWN AND L. D. HAYWARD

ABSTRACT

From a 0.368*M* solution of d-mannitol hexanitrate in pyridine at $30 \pm 5^\circ\text{C}$. a gas consisting of nitric oxide, nitrous oxide, and nitrogen was evolved and d-mannitol-1,2,4,5,6-pentanitrate and pyridinium nitrate were recovered after dilution with water. The amount and composition of the gas mixture were sensitive to traces of moisture in the pyridine. Establishment of a material balance for the reaction indicated that approximately two moles of pyridine suffered ring cleavage while 0.25 mole of hexanitrate was completely denitrated and 0.75 mole of pentanitrate was formed. Some features of the mechanism of the denitration reaction are discussed.

In earlier papers it was shown that pyridine caused selective partial denitration of dulcitol (22) and d-mannitol (18) hexanitrates; the corresponding pentanitrates were recovered in 67–73% yield and identified as the 3-hydroxy derivatives in each case. Elrick and collaborators have recently confirmed these results with d-mannitol hexanitrate and have also shown that treatment with an aqueous acetone solution of ammonium carbonate gave a similar yield of the same d-mannitol pentanitrate (11).

The pyridine denitration amounted to the replacement of nitronium ion by a proton at the oxygen atom of carbon 3 in the hexitol hexanitrate since no racemization or inversion of the asymmetric centers occurred. In the present research the nonhexitol products of the reaction of pyridine with d-mannitol hexanitrate were explored in an attempt to reveal further details of this unusual selective reaction (32).

Pure d-mannitol hexanitrate dissolved readily in pyridine in a molar ratio of 1:34 to give an initially colorless solution which rapidly turned yellow and then deep red while external cooling was required during the first hour to maintain the temperature below 35°C . When the reaction was carried out in an open vessel (Runs F and G), small bubbles of gas rapidly rose through the solution and a red-brown vapor collected in the upper part of the flask. After the solution was left for 24 hr. at room temperature a thin film of colorless crystals was observed on the inner walls of the flask above the solution. This material was collected and identified as pyridinium nitrate. In other runs (A to E), contact with the atmosphere was avoided during the reaction and the temperature maintained at $30 \pm 2^\circ\text{C}$. by combining the reactants in the

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Contribution from the Department of Chemistry, University of British Columbia, Vancouver, B.C. This paper is based on a thesis submitted by J. R. Brown in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, April, 1958, and was presented in part before the second Western Regional Conference, the Chemical Institute of Canada, Vancouver, September, 1954.

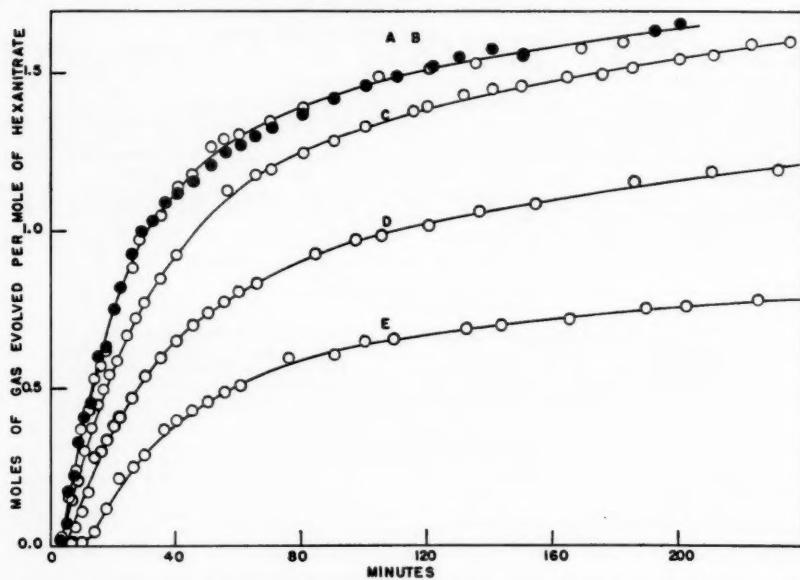


FIG. 1. Gas evolved in the denitration of D-mannitol hexanitrate with dried (A, B) and with moist (C, D, E) pyridine.

Toricellian vacuum of a water-cooled du Pont nitrometer, and in these cases the gas evolved was colorless and no crystals of pyridinium nitrate appeared.

The volume of the gas evolved in the nitrometer was measured at intervals, corrected for the vapor pressure of pyridine (34), and plotted against time (Fig. 1, Runs A and B). Extrapolation of the nearly linear, later portion of these rate plots to zero time indicated the production of about 1.33 moles of gas per mole of hexanitrate in the initial vigorous reaction. The addition of small amounts of water to the pyridine considerably reduced the amount of

TABLE I
COMPOSITION OF THE GAS EVOLVED FROM A 0.368 M SOLUTION OF D-MANNITOL HEXANITRATE
IN PYRIDINE AT 30°C.

Run	Time of reaction (min.)	Composition of the gas evolved			
		% N ₂ O	% NO	% N ₂	% Pyridine
A ^a	180	63.6	16.5	17.4	2.5
		63.3	16.3	17.9	2.5
B ^a	200	62.1	17.5	18.0	2.4
C ^b	240	61.1	18.1	18.2	2.5
D ^c	240	58.6	19.3	19.4	2.8
E ^d	240	56.5	18.5	22.2	2.8

^aPyridine was freshly distilled over barium oxide.

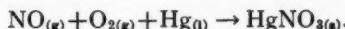
^bDried pyridine was exposed to the laboratory atmosphere for three minutes before use.

^cWater, 0.17% by weight, was added to the pyridine.

^dWater, 0.34% by weight, was added to the pyridine.

gas evolved (Fig. 1, Runs C, D, and E). The compositions of the gaseous products collected during four hours in each of Runs A to E are compared in Table I.

Chemical (20) and mass-spectrometric (17) methods for determining nitrous oxide, nitric oxide, and nitrogen in admixture have but recently been reported; the procedure developed in the present case appeared to be new and although probably less accurate, was considerably more straightforward than the above. Nitric oxide was determined in the evolved gas by mixing it with an excess of pure oxygen and exposing the mixture to a fine stream of mercury droplets until it became colorless and constant in volume. Previous reports of this reaction (10, 23, 24) were qualitative in nature; our experiments with samples of the pure gases showed the reaction to be quantitative and to be represented by the following equation at room temperature:



After removal of the nitric oxide the remaining gas was analyzed for nitrous oxide, carbon dioxide, and the known excess of oxygen in an Orsat apparatus (28) and for nitrogen by gas-density measurements on the nonabsorbable residual gas (19, 28). Appropriate corrections were made for the pyridine vapor and its coabsorption with the nitrous oxide. The over-all accuracy of the method was assessed at 1.5% with known samples of the individual gases.

Crystalline D-mannitol-1,2,4,5,6-pentanitrate was recovered from the pyridine solutions as previously described (18) when these were diluted with water; the yields obtained at different reaction times are shown in Table II.

TABLE II
YIELD OF D-MANNITOL-1,2,4,5,6-PENTANITRATE WITH
DRIED AND WITH MOIST PYRIDINE

Run	Time of reaction (min.)	% Yield
A	180	70.8
B	200	71.6
C	240	73.0
D ^a	240	77.8
E ^a	240	76.5
F ^b	1080	73.0
G ^b	1440	69.0

^aWater was added to the pyridine before reaction, see Table I.

^bThe reaction mixture was exposed to air (18).

An orange-brown, partially crystalline residue, 42% of the weight of the hexanitrate used, was obtained by careful evaporation of an aliquot of the yellow aqueous filtrate, and crystalline pyridinium nitrate (31% of the residue) was isolated from this solid by adsorption of the colored material on charcoal. Paper chromatography of the aqueous filtrate indicated about 14 components to be present, but no clear-cut separation of these substances could be achieved by fractional crystallization, solvent partition, dialysis, adsorption chromatography on silica gel, or by treatment with an anion exchange resin. Attempts

to separate pyridine quantitatively from the residue by precipitation from acetic acid solution as the perchlorate salt (4) or from aqueous solution as the copper thiocyanate complex (30) were unsuccessful and nitrogen analyses for nitrate were hampered by the presence of pyridine.

Potentiometric titration of aliquots of the aqueous pyridine filtrate first with alkali and then with acid revealed the concentration of *bound* and of *free* pyridine. The accuracy of this method was assessed as 1.1% with suitable aqueous solutions containing pyridine and pyridinium nitrate. *Bound* pyridine was recorded as equivalent to nitrate ion and the sum of *bound* and *free* pyridine as unreacted pyridine. These assumptions were supported by the actual isolation of 0.41 mole of pyridinium nitrate per mole of hexanitrate and by the agreement between the pH values measured potentiometrically at the beginning of the titration (7.57) and at the equivalence points (10.1, 4.2) and those calculated from the apparent ionization constant (pK_b , 7.82) (26) measured in the known solution (initial pH, 7.55; calculated at equivalence points: 10.0, 3.3). A summary of the analyses of the four-hour runs C, D, and E is given in Table III.

TABLE III
COMPONENTS IN THE REACTION OF PYRIDINE WITH D-MANNITOL HEXANITRATE

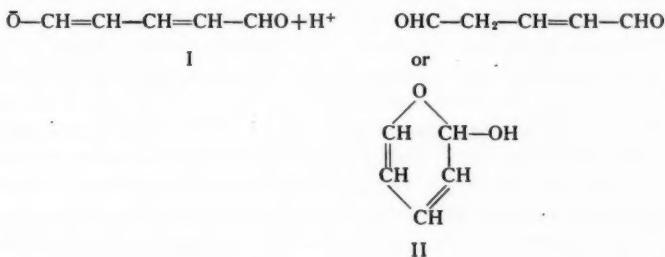
	Run C	Run D	Run E
<i>Reactants (moles)</i>			
p-mannitol hexanitrate	1.00	1.00	1.00
Pyridine	40.5	40.5	40.5
Water	Trace	0.25	0.50
<i>Elementary composition of reactants (gm-atoms)</i>			
C	208.5	208.5	208.5
H	210.5	211.0	211.5
O	18.0	18.3	18.5
N	46.5	46.5	46.5
<i>Products (moles)</i>			
p-mannitol pentanitrate	0.73	0.77	0.76
Pyridine unreacted ^a	38.4	38.5	38.9
Nitrous oxide ^b	1.24	0.94	0.67
Nitric oxide	0.30	0.24	0.15
Nitrogen gas	0.30	0.24	0.18
Nitrate ion	1.63	1.66	1.73
<i>Elementary composition of products identified (gm-atoms)</i>			
C	196.4	197.1	199.1
H	198.6	199.4	201.3
O	18.1	18.4	18.3
N	47.1	46.6	46.3

^aCorrected for losses in manipulations.

^bIncluding nitrous oxide dissolved in the pyridine (29).

As shown in Table III the total nitrogen and oxygen content of the reactants was accounted for, within the experimental error, as mannitol pentanitrate, nitrogen, nitrogen oxides, nitrate ion, and unreacted pyridine. The mannitol hexanitrate not represented by the pentanitrate recovered, an average of 0.25 mole, was therefore completely denitrated in the aqueous solution. One mole

of hexanitrate yielded on the average 0.75 mole of pentanitrate while approximately 2.0 moles of pyridine disappeared. That some of this pyridine suffered ring cleavage in the initial vigorous reaction was certain since, in Runs A, B, and C, the total nitrogen content of the pentanitrate and gases isolated, excluding that of nitrate ion and pyridine, exceeded the nitrogen content of the original amount of hexanitrate by 0.88, 1.19, and 1.03 gm-atoms per mole respectively. In Runs D and E these figures were substantially lowered (0.45 and -0.35) by the presence of water in the pyridine. The material balance calculated for the three runs (Table III) indicated that the unidentified, water-soluble, and dialyzable products were probably nitrogen-free and approximated to the composition $C_xH_x(OH)_y$ of a mixture of unsaturated aldehydes and alcohols of low molecular weight. A possible major component was glutaconaldehyde (I and II), $C_5H_6O_2$, which has been shown by Zincke and others (5, 13, 14, 36, 37) to be formed by ring opening of pyridine under salt-forming and oxidizing conditions and to have indicator properties, existing in basic media as the dark red enolate ion (I) and in acid solution as



the yellow-brown dialdehyde (II). The aqueous pyridine denitration solutions showed a reversible change in color from pale yellow to orange with alteration of pH from 4 to 10, but attempts to isolate the dianilide of glutaconaldehyde (12) were unsuccessful and were hampered by the presence of pyridinium nitrate. Evaporation of the aqueous pyridine solution in the presence of excess potassium hydroxide left a dark, tarry, pyridine-free substance. Steam distillation of an alkaline solution of glutaconaldehyde was shown by Baumgarten and Glatzel (6) to cause decomposition of the dialdehyde to acetaldehyde, formic acid, crotonaldehyde, and other fragments.

Since several reaction products, amounting to 4 to 5% of the carbon and hydrogen content of the reactants, remained unidentified, the over-all mechanism for the denitration reaction was not obvious; some salient features of the reaction, however, were indicated:

(a) The source of the proton substituted for nitronium ion in the nitryl-oxy-fission (3) appeared to be traces of active hydrogen remaining in the pyridine after distillation from barium oxide. Nitronium ion substitution on carbon atoms of the pyridine nucleus was ruled out as the source of the proton since pyridine has been shown to stubbornly resist such substitution (16, 27). Tanberg (33) showed that samples of pyridine distilled from barium oxide

contained 0.013 to 0.028% by weight active hydrogen and Zerewitinoff (35) considered that this active hydrogen might have been present as dihydro-pyridine formed in the drying operation. The yield of pentanitrate obtained in Run C would require 0.028% active hydrogen to be retained in the pyridine; in Runs A and B the pyridine was exposed to the moist laboratory air for shorter periods of time and the yield of pentanitrate was lowered (Table II). Addition of small amounts of water (0.17 and 0.34% by weight) in Runs D and E considerably reduced the amounts of gas evolved but only slightly increased the yield of pentanitrate.

(b) Nitrogen cleaved from the pyridine ring in the anhydrous reaction appeared in part in the gaseous form, the proportion so evolved decreased with increasing moisture content although the amount of pyridine ring-opened was only slightly reduced by added water. Freytag (14, 15) showed that hygroscopically absorbed moisture reacted with pyridine to form pyridinium hydroxide which subsequently suffered ring opening, slowly in the dark, more rapidly in sunlight and in the presence of nitrate ion, to give the colored ammonium salt of the enolic glutaconaldehyde (I), "photopyridine". Lane (21) has reported colored polymeric material to be formed in addition to pyridinium nitrate and alkenes when pyridine was treated with some simple alkyl secondary and tertiary nitrate esters at reflux temperature.

(c) Nitrogen dioxide, if released from the hexanitrate, could be expected to form first an addition compound with the pyridine of the type described by Spencer (31) and others (1, 9) and this complex would then undergo oxidation-reduction reactions (9) to give the gaseous products observed.

(d) The 0.25 mole of hexanitrate not recovered in the form of pentanitrate was rendered soluble in water and, from the nitrogen balance (Table III), was probably denitrated to a tetranitrate stage in the first vigorous reaction with dried pyridine and then completely saponified during the titration of the aqueous pyridine solution with 0.2 N alkali.

It is of interest that in the partial denitration of other polynitrates (19, 28) the presence of free hydroxylamine in the pyridine inhibited the color formation, caused the evolution of gaseous nitrogen only, and increased the rate of reaction. The formation of the colorless dioxime of glutaconaldehyde (7) might account for the very slow development of color in those reactions.

EXPERIMENTAL

Materials and Methods

Pure D-mannitol-1,2,3,4,5,6-hexanitrate was prepared as described previously (18). The usual precautions (18, 19, 22) were observed in handling this high explosive and its derivatives.

Analytical reagent grade pyridine supplied by the British Drug Houses was dried by distilling over anhydrous barium oxide with care to avoid exposure to moist air.

Gas Evolved from D-Mannitol Hexanitrate and Pyridine

Pure, finely divided mannitol hexanitrate, 2.500 gm., was placed in the cup

of the reaction vessel of a du Pont nitrometer which was fitted with a thermometer well and water-cooling jacket and connected to two gas burettes by a three-way stopcock. The nitrate was quickly washed into the reaction chamber with pyridine, 15.0 ml., with care to prevent the entry of air, and the volume and temperature of the colorless gas evolved were noted at two to four minute intervals. The rate plots with the most carefully dried pyridine were closely grouped (Fig. 1, Runs A and B) and were corrected for the vapor pressure of pyridine (34). Similar experiments were carried out with pyridine to which water had been added from a graduated pipette (Fig. 1, Runs D and E) and with pyridine previously exposed to the moist air of the laboratory for three minutes before use (Fig. 1, Run C).

Admission of air or oxygen to a sample of the evolved gas caused the immediate appearance of red-brown nitrogen dioxide indicating nitric oxide to be present. The brown gas reacted slowly with the surface of the confining mercury forming a gray to white powder. When a continually renewed, fresh surface of mercury was exposed to the gas mixture by adjusting the mercury levelling bulbs so that a fine stream of mercury droplets flowed through it, the color of the gas disappeared and the residual volume became constant in about two hours at room temperature. To test the value of this reaction as a means of determining nitric oxide, 16.20 ml. of nitric oxide was generated by the nitrometer reaction from pure potassium nitrate and mixed with 16.40 ml. of dry oxygen (99.0% soluble in alkaline pyrogallol) at 757.0 mm. and 20.5°C. The mercury stream was passed through this mixture and the residual volume of colorless gas was 0.30 ml. after two hours indicating that the reaction was 99.4% complete. The grayish white powder trapped by the mercury against the walls of the gas burette partially dissolved in water to give an acid solution. It dissolved readily in dilute nitric acid and appeared to be mercurous nitrate (23, Vol. 4, p. 987).

After four hours' reaction time the pyridine denitration solution was removed from the nitrometer chamber which was flushed with pyridine (3.00 ml.) and then with water (10 ml.) and dried with acetone. Dry oxygen, approximately one half the volume of the evolved gas, was then admitted through the chamber to the burette and the mixed gases were treated with mercury as before. The volume of the colorless residual gas became constant in about two hours and the gas was then analyzed in an Orsat apparatus equipped with pipettes containing 95% ethanol, 40% potassium hydroxide, and alkaline pyrogallol solutions for absorption of nitrous oxide (28), ethanol vapor and carbon dioxide, and oxygen respectively. The percentage of nitrous oxide was given by $aV_2/V_1 - p 100/P$, of nitrogen by bV_2/V_1 , and of nitric oxide by $100 - (a+b)V_2/V_1$, where a and b were respectively the percentage of the mercury-and-oxygen-treated gas absorbed by ethanol and 40% potassium hydroxide, and the percentage of the nonabsorbable gas. V_1 was the volume of the gas before admission of oxygen, V_2 the volume of the gas after treatment with oxygen and mercury, p the vapor pressure of pyridine (34), and P the atmospheric pressure. The nonabsorbable gas was found to have a molecular weight of 29.1 ± 0.5 (average of six experiments) by the method of Daniels,

Mathews, and Williams (8) and was assumed to be nitrogen (19, 28); any carbon monoxide present in the evolved gas would have been oxidized at room temperature to the dioxide by the nitrogen dioxide. In the analysis of the oxygen-and-mercury-treated gas a repass through the ethanol pipette established that the loss in volume of the gas (<1.5%) on passage through the potassium hydroxide solution was probably due to absorption of ethanol vapor and not to acid gases. The results of these analyses are shown in Table I. A sample of commercial nitrous oxide was found to be 98.5% soluble in 95% ethanol, the absorption requiring 90 min.

Isolation of D-Mannitol-1,2,4,5,6-pentanitrate

The reaction mixture removed from the nitrometer was poured into water, 200 ml., contained in a ground-glass stoppered flask. The pyridine and water washings were added and after the solution had stood for two hours the precipitation of solid material was complete. The crystalline, nearly colorless product was recovered on a fritted glass crucible, washed thoroughly with water, and dried *in vacuo*. After two recrystallizations from aqueous ethanol the pure D-mannitol-1,2,4,5,6-pentanitrate melted correctly at 81–82°C. (11, 18). This melting point was not altered by further recrystallization from carbon tetrachloride. The specific rotation in alcohol was +47.7° ($c, 4.426$).* The yields of crude pentanitrate obtained at several different reaction times with dried and moist pyridine are given in Table II.

The Aqueous Pyridine Solution from the Denitration Reaction

The combined filtrate and washings from the denitration of 5.00 gm. of hexanitrate (Run F) were evaporated to dryness *in vacuo*. The solid, odorless, orange-brown residue contained some crystals and weighed 2.61 gm. From Run G 2.1 gm. of the residue was similarly obtained. This material was readily soluble in water, methanol, ethanol, and acetic acid and to the extent of about 75% in boiling acetone. It was slightly soluble in ether, benzene, and petroleum ether.

A portion of the solid residue, 0.78 gm., dissolved in 50 ml. of water was heated to boiling with 1 gm. of activated charcoal and filtered through Kieselguhr. Evaporation of the slightly yellow filtrate and recrystallization of the residual product from acetone gave 0.24 gm. of colorless, odorless needles melting at 115.0–116.2°. The substance was pyridinium nitrate since it immediately produced a strong odor of pyridine on contact with caustic solution and did not depress the melting point (115.5–117.2°) of authentic pyridinium nitrate prepared from pyridine and yellow fuming nitric acid (2, 25). Crude pyridinium nitrate, 0.12 gm., was also recovered in Run G from the inner walls of the reaction flask which had been exposed to the laboratory atmosphere during the denitration. Further small amounts of pyridinium nitrate were obtained by fractional crystallization of an acetone extract of the residue.

Other attempts to fractionally crystallize or partition the residue with a variety of solvents gave only highly colored amorphous products. A sample of the residue (*ca.* 5 mgm.) was chromatographed on paper for 24 hr. by the

*An incorrect value of +43.6° was reported earlier (18).

descending technique with butanol-water-ethanol-ammonia (40: 49: 10: 1) as irrigating solvent. The dried chromatogram was inspected under ultraviolet light, which revealed 14 distinct spots ranging in color from pink to blue with R_f values from 0.02 to 0.90. D-Mannitol pentanitrate and pyridinium nitrate did not fluoresce under the same conditions. Adsorption chromatography of the acetone extract of 0.8 gm. of residue on a column of unactivated silica gel (80-115 mesh, 1.3×52 cm.) with acetone followed by methanol as eluting solvents gave six separate fractions detected by diphenylamine reagent, each of which was amorphous and yellow to orange in color and was not investigated further.

To 0.62 gm. of pyridinium nitrate dissolved in 10 ml. of glacial acetic acid was added a 1 *N* solution of perchloric acid in acetic acid until precipitation of the colorless pyridinium perchlorate (14) was complete. The dried precipitate (0.75 gm.) represented 98% of the pyridinium nitrate. An attempt to precipitate pyridinium perchlorate from a glacial acetic acid solution of the residue (0.70 gm.) gave a dark colored solid product (0.73 gm.) which was not investigated further. Dialysis against water of a solution of 0.80 gm. of the residue in 100 ml. of water contained in a cellophane bag caused all but 0.01 mgm. of the residue to move into the dialyzing liquid in 24 hr. The brown product from the evaporated dialyzate could not be crystallized. Amberlite I-R-45 anion exchange resin, 20 gm., completely removed nitrate ion (diphenylamine test) from a solution of 1 gm. of pyridinium nitrate in 100 ml. of water. When 0.68 gm. of the residue was treated in a similar manner with the exchange resin, and the treated solution was evaporated to dryness, 0.11 gm. of a hard, amorphous, dark brown solid remained which gave a paper chromatogram similar to that of the untreated residue, but showing only nine separate spots under ultraviolet light.

A portion of the residue, 1.31 gm., was dissolved in anhydrous methanol, 50 ml., treated with sodium hydroxide pellets, 0.4 gm., and warmed with stirring on the steam bath for five minutes. When all the hydroxide had dissolved the solution became turbid and a fine brown precipitate separated while the solution gave off a distinct odor of pyridine. Concentrated hydrochloric acid (1.70 ml.; d., 1.18) was then added with stirring and the solution once more became clear and yellow in color. Aniline, 2.00 ml., was added and the solution gradually became deep cherry-red in color. Evaporation of the solution left a large amount of colorless crystalline product covered with a sticky, deep-red sirup which could not be induced to crystallize. N-(2,4-Dinitro-)-phenylpyridinium hydrochloride in ethanol solution gave an immediate precipitate of the dianilide hydrochloride of glutaconaldehyde (12) as cherry-red needles (44% of theory) when treated with hydrochloric acid and aniline under the same conditions.

Titrimetric Estimation of Pyridine and Nitrate in the Reaction Products

Twenty-five-milliliter aliquots of a 250 ml. aqueous solution containing 1.340 gm. of pyridinium nitrate and 18.2 gm. of pyridine were titrated first with 0.2 *N* potassium hydroxide solution for estimation of nitrate ion and then

with 0.6 N sulphuric acid for estimation of total pyridine (*free* pyridine added plus *bound* pyridine released from the pyridinium nitrate). The end points, detected with a Beckman model G pH-meter, occurred at pH 10.23 for the alkali titration and at pH 4.13 for the acid titration and had a sharpness of about 0.16 pH units per 0.20 ml. at the maxima. Found: pyridinium nitrate, 0.134, 0.135 gm. (100.3%); pyridine, 1.81, 1.81 gm. (99.5%).

Each filtrate from the isolation of D-mannitol pentanitrate in Runs C, D, and E was combined with the water washings and made up to 250 ml. and aliquots of these solutions were titrated by the above procedure. The value from the alkali titration was recorded as nitrate ion concentration and that from the acid titration as concentration of unreacted pyridine in Table III. Losses of pyridine in the manipulations were estimated at 1.1% by carrying out the procedure of denitration with a pyridine blank.

Evaporation of 25-ml. aliquots of the denitration solutions from Runs C, D, and E after addition of a measured excess of potassium hydroxide left 0.097, 0.046, and 0.102 gm. of dark amorphous residues respectively.

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INTENSITY IN THE RAMAN EFFECT

IV. RAMAN INTENSITY SUM RULES AND FREQUENCY ASSIGNMENTS FOR CH₃CN, CD₃CN, CH₃CCl₃, AND CD₃CCl₃¹

By J. C. EVANS² AND H. J. BERNSTEIN

ABSTRACT

The standard intensities of the Raman bands of CH₃CN, CD₃CN, CH₃CCl₃, and CD₃CCl₃ have been obtained for the liquids with a photoelectric, grating spectrometer. The intensity sum rules for isotopic homologues are valid within the experimental error. The infrared spectra of CD₃CN and CD₃CCl₃ have been obtained in the liquid phase and in the vapor phase. A definitive assignment of ν_{11(e)} has been made for methyl chloroform.

In Paper III (1) of this series the theoretical rules relating the intensities of vibrational Raman bands in isotopic molecules were applied to benzene and its deuterium substituted homologues. Within the experimental uncertainty the rules were found to be valid. Further intensity data have been obtained and tests of the rules have been made for CH₃CN and CD₃CN and for CH₃CCl₃ and CD₃CCl₃.

The vibrational spectra of the two deuterium substituted molecules have not been reported previously, but methyl cyanide (10, 11) and methyl chloroform (8) have been studied extensively. However, there are available only qualitative values for the depolarization ratios of the Raman bands of CH₃CN (3) and only 10 of the 12 fundamental modes of CH₃CCl₃ are well-established. Of the two remaining modes one is inactive in both Raman and infrared, while the other has been assigned differently by various authors (8). The Raman spectrum of CD₃CCl₃ enabled this last difficulty to be resolved.

EXPERIMENTAL

The CH₃CN and CH₃CCl₃ were Eastman Kodak samples; they were fractionally distilled. The methods of preparing the deuterium substituted compounds will be described: CD₃CN (6), CD₃CCl₃ (7).

A White, grating Raman spectrometer with photoelectric recording (12) and a Perkin Elmer model 112 double pass spectrometer were used to record the spectra. Depolarization ratio measurements were made (5) and corrected for convergence error (9). Standard intensities of scattering per molecule referred to the 458 cm.⁻¹ band of CCl₄ were obtained (2).

The observed Raman spectra and the corrected depolarization ratios for CH₃CN and CD₃CN are summarized in Table I, and the infrared data for CD₃CN are given in Table II. Figs. 1 and 2 illustrate the spectra. The doubtful Raman band reported at 1124 cm.⁻¹ in previous investigations on CH₃CN was not observed here. In CD₃CN, ν₁, ν₂, 2ν₈, and 2ν₆ appear to be in Fermi resonance.

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TABLE I

RAMAN SPECTRA OF CH₃CN AND CD₃CN IN THE LIQUID STATE

Assignment	CH ₃ CN		CD ₃ CN	
	cm. ⁻¹	Corrected depol. ratio	cm. ⁻¹	Corrected depol. ratio
$\nu_5(e)$	3001	0.86	~2258	Overlapped by ν_2
$\nu_1(a_1)$	2941	0.09	2112	0.12
$2\nu_5(A_1+E)$	2882	P	2057	0.13
$\nu_2+\nu_4(A_1)$	2289	0.26	—	F.R.
$\nu_2(a_1)$	2248	0.20	2258	0.29
$2\nu_3(A_1)$	—		2209	0.44
$\nu_8(e)$	1443	0.85	1041	0.86
$\nu_3(a_1)$	1371	0.52	1103	0.70
$\nu_4(a_1)$	919	0.17	834	0.23
$2\nu_8(A_1+E)$	750	0.51	684	0.43
$\nu_7-\nu_5(A_1+A_2+E)$	674	0.46	—	
$\nu_9(E)$	379	0.86	348	0.86

In this and in the other tables, wave number values are corrected to vacuum.

*Fermi resonance.

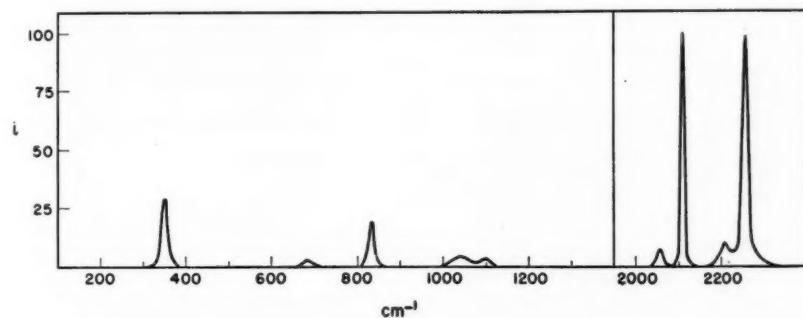


FIG. 1. The observed Raman spectrum of CD₃CN. The intensity of the band with greatest peak height is 100. Slits were 6.5 cm.⁻¹ in the 3000 cm.⁻¹ region and 7.5 cm.⁻¹ in the region 0–1600 cm.⁻¹.

ance. Several minor features in the infrared spectrum of CD₃CN remain to be explained. The band at 1375 cm.⁻¹ in the vapor was not observed in the liquid spectrum while the band at 2692 cm.⁻¹ in the liquid has no simple explanation. The band at 1246 cm.⁻¹ in the vapor and one of the two bands at 1266 and 1282 cm.⁻¹ in the liquid seem to correspond to 4 ν_8 . (Some support for this assignment is that ν_8 also shifts to higher wave number from vapor to liquid.) The assignments of the fundamentals and of the other observed bands are straightforward.

TABLE II
INFRARED SPECTRUM OF CD₃CN BETWEEN 300 AND 3400 CM.⁻¹

Wave number		Assignment*
Liquid	Vapor	
3376 vw	3380	$\nu_2 + \nu_3 = 3361 (A_1)$
3286 vw	~3300	$\nu_2 + \nu_6 = 3299 (E)$
3200 vvw	—	$\nu_1 + \nu_3 = 3215 (A_1)$
3096 w	3115	$\nu_2 + \nu_7 = 3108 (E)$ or $\nu_2 + \nu_4 = 3092 (A_1)$
2965 vw	2985	$\nu_1 + \nu_7 = 2962 (E)$
2962 w	—	
2607 w	2600	$\nu_2 + \nu_8 = 2606 (E)$
2263 s	{ 2289 2279 2270 (overlapped)}	$\nu_2(a_1)$ $\nu_2(e)$
2212 vvw	—	$2\nu_3 = 2206 (A_1)$
2116 w	{ 2137 2126 2117	$\nu_1(a_1)$
2059 w	{ 2088 2073 2065	$2\nu_6 = 2082 (A_1+E)$
1945 vw	1950	$\nu_3 + \nu_7 = 1953 (E)$
1931 vw	~1930	$\nu_3 + \nu_4 = 1937 (A_1)$
1884 vw	~1900	$\nu_7 + \nu_6 = 1891 (A_1 + A_2 + E)$
	1375 w	$\nu_6 + \nu_8 = 1389 (A_1 + A_2 + E)$
1282 w	~1246	$\} 4\nu_8 \approx 1300 (A_1+2E)$
1266 w		
1197 m	{ 1181 1166	$\nu_7 + \nu_8 = 1198 (A_1 + A_2 + E)$
1103 m	~1115 (overlapped by ν_6)	$\nu_3(a_1)$
1039 vs	Resolved: center 1052	$\nu_6(e)$
850 m	~850 (overlapped by ν_4)	$\nu_7(e)$
833 vs	{ ~845 833 820	$\nu_4(a_1)$
687 w	{ 670 ? (overlapped by CO ₂) 645	$2\nu_8 = 696 (A_1+E)$
348 m	335	$\nu_8(e)$

*Liquid phase data were used in computing the frequencies in the last column of this table and Table III.

The Raman and infrared data for CD₃CCl₃ are collected in Table III and are illustrated in Figs. 3 and 4. Corresponding to the band at 343 cm.⁻¹ in the liquid phase spectrum of CH₃CCl₃, there are in CD₃CCl₃ two bands, 335 (*a*₁) and 315 (*e*). This latter band is the controversial *e*-type mode which in CH₃CCl₃ must be at 343 cm.⁻¹ in the liquid and at 350 cm.⁻¹ in the vapor. Pitzer and Hollenberg's suggestion (8) (which is based on the observed combination tones in the far infrared) that the 350 cm.⁻¹ band in CH₃CCl₃ vapor is composed of an *a*₁ type and an *e*-type band is therefore confirmed.

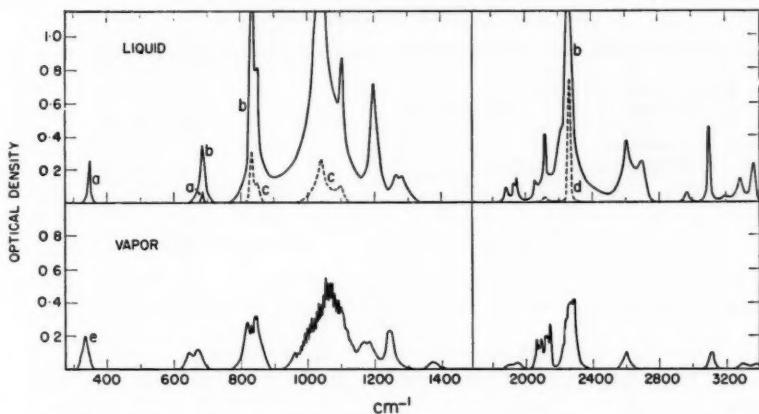


FIG. 2. The infrared spectrum of CD_3CN .
 Liquid: *a*, capillary film; *b*, 0.1 mm. film; *c*, another capillary film; *d*, another capillary film.
 Vapor: *e*, 6 cm. cell at $60^\circ\text{C}.$; vapor pressure $\sim 370 \text{ mm}$. The remainder of the spectrum was obtained with a 1 meter cell at $20^\circ\text{C}.$; vapor pressure $\sim 70 \text{ mm}$.

TABLE III
 EXPERIMENTAL DATA FOR CD_3CCl_3

Raman data (liquid phase)		Infrared data		Assignment
cm. ⁻¹	Corrected depol. ratio	Liquid	Vapor	
		3426 vvvw	3445	$3\nu_2 = 3420 (A_1)$
		3301 vvw	3307	$2\nu_2 + \nu_8 = 3323 (E)$ $\nu_7 + \nu_8 = 3299 (A_1 + A_2 + E)$
		3233 vvw	3242	$\nu_1 + \nu_2 = 3269 (A_1)$ $\nu_3 + \nu_7 = 3230 (E)$
		3178 vvw	3190	$\nu_1 + \nu_8 = 3175 (E)$ $\nu_7 + \nu_9 = 3172 (A_1 + A_2 + E)$ $2\nu_2 + \nu_9 = 3196 (E)$
		3054 vvw	3064	$\nu_1 + \nu_9 = 3048 (E)$ $2\nu_2 + \nu_3 = 3062 (A_1)$
		3008 vvw } Broad		$2\nu_8 + \nu_9 = 3004 (A_1 + A_2 + 2E)$
		2974 vvw } ill-defined		$\nu_2 + \nu_4 + \nu_{12} = 2994 (E)$
		2929 vvw } absorption		$2\nu_2 + \nu_{10} = 2937 (E)$
2277	0.19	2280 vw	—	$2\nu_2 = 2274 (A_1)$
2256	0.86	2257 vw	2265	$\nu_7(e); \nu (\text{CD}_3)$
2150	0.24			$\nu_8 + \nu_9 + \nu_{12} = 2179 (A_1 + A_2 + 3E)$
2132	0.10	2136 vw	{ 2152 2143 2135	$\nu_1(a_1); \nu (\text{CD}_3)$
2099	0.08	2103 vw	—	$\nu_2 + \nu_3 = 2111 (A_1)$
2068	0.13	2072 vvw	—	$2\nu_2 = 2088 (A_1 + E)$
		1312 vw	1325	$2\nu_{10} = 1314 (A_1 + E)$
		1280 vw	1285	$\nu_3 + \nu_{11} = 1293 (E)$
		1260 vw	—	$\nu_8 + \nu_{12} = 1275 (A_1 + A_2 + E)$
		1165 w sh	1170	$\nu_4 + \nu_{10} = 1160 (E)$
1137	0.68	1140 vs	{ 1153 1145 1138	$\nu_2 (a_1); \delta (\text{CD}_3)$
		1120 vw sh	—	$\nu_10 + \nu_{12} + \nu_{12} = 1127 (A_1 + A_2 + 2E)$

TABLE III (*Concluded*)

		Raman data (liquid phase)	Infrared data		Assignment
	cm. ⁻¹	Corrected depol. ratio	Liquid	Vapor	
			1105 vw	$\begin{cases} ? \\ 1110 \\ 1102 \end{cases}$	$\nu_6 + \nu_9 \sim 1116 (E)$
1043	0.86		1044 m	$\begin{cases} 1059 \\ 1050 \\ 1042 \end{cases}$	$\nu_8 (e); \delta (\text{CD}_3)$
			1013 vw 992 vw sh	$\begin{cases} 1020 \\ 1000 \end{cases}$	$2\nu_4 = 1014 (A_1)$ $\nu_5 + \nu_{10} = 992 (E)$
974	0.50		976 m	$\begin{cases} 977 \\ 967 \end{cases}$	$\nu_3 (a_1); \nu (c - c)$
			943 m sh	950	$\nu_4 + \nu_{12} + \nu_6 \sim 940 (E)$
916	0.86		919 vs	$\begin{cases} 932 \\ 925 \end{cases}$	$\nu_9 (e); \delta (\text{CD}_3)$
			893 vw	896	$\nu_{10} + \nu_{12} = 888 (A_1 + A_2 + E)$
			866 m	$\begin{cases} 876 \\ 869 \end{cases}$	$\nu_6 + \nu_{10} \sim 857 (E)$
			812 vw 790 vvw 727 w	$\begin{cases} 818 \\ 795 \\ 728 \end{cases}$	$\nu_4 + \nu_{11} = 823 (E)$ $2\nu_{12} + \nu_6 = 797 (A_1 + E)$ $\nu_4 + \nu_{12} = 736 (E)$
657	0.86		605 vvw 580 vvw	$\begin{cases} 700 w \\ 665 vvs \\ \vdots \end{cases}$	$2\nu_5 = 676 (A_1)$ $\nu_{10} (e); \nu (\text{CCl}_3)$ $2\nu_{11} = 630 (A_1 + E)$ $\nu_9 - \nu_5 = 581 (E)$ $\nu_{11} + \nu_{12} = 546 (A_1, E)$
553 vvw	P		—	—	
503	0.09		506 s	$\begin{cases} 516 \\ 507 \\ 497 \end{cases}$	$\nu_4 (a_1); \nu (\text{CCl}_3)$
445 vvw	P?		466 vvw 413 vvw	— —	$2\nu_{12} = 462 (A_1 + E)$ $\nu_6 + \nu_{12} \sim 440 (E)$ $2\nu_5 \sim 420 (A_1)$ $\nu_9 - (\nu_{11} + \nu_{12}) = 366 (A_1 + A_2 + 3E)$
364 vvw	P		—	—	
335	0.40		338 m	$\begin{cases} 347 \\ 338 \\ 327 \end{cases}$	$\nu_5 (a_1); \delta (\text{CCl}_3)$
315	0.86		317 m	$\begin{cases} 327 \\ 317 \end{cases}$	$\nu_{11} (e); \delta (\text{CCl}_3)$
231	0.86				$\nu_{12} (e); \delta (\text{CCl}_3)$

In CD_3CCl_3 , $2\nu_5$, and $\nu_2 + \nu_3$, which are presumably in Fermi resonance with ν_1 , appear in the liquid spectra but are absent from the infrared vapor spectrum. This may be due to the removal or reduction of Fermi resonance by the separation of levels which are influenced differently by intermolecular interaction. The band at 2280 cm.^{-1} in the liquid, assigned as $2\nu_2$, is also absent from the spectrum of the vapor.

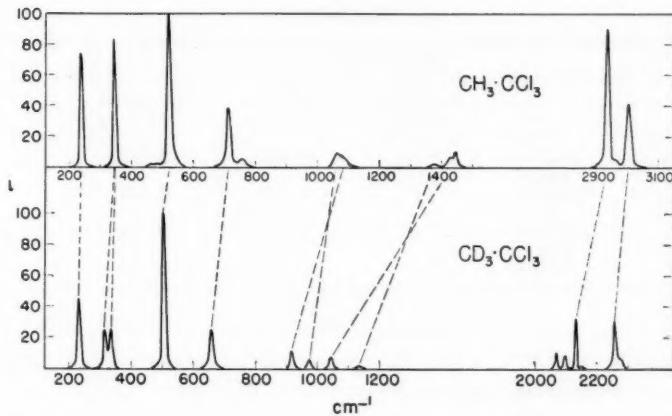


FIG. 3. The observed Raman spectra of CH_3CCl_3 and CD_3CCl_3 . In each spectrum the band with greatest peak height is 100; the two scales are therefore not identical. Slits were 5 cm^{-1} in the 3000 cm^{-1} region and 6.5 cm^{-1} in the region $0-1600 \text{ cm}^{-1}$.

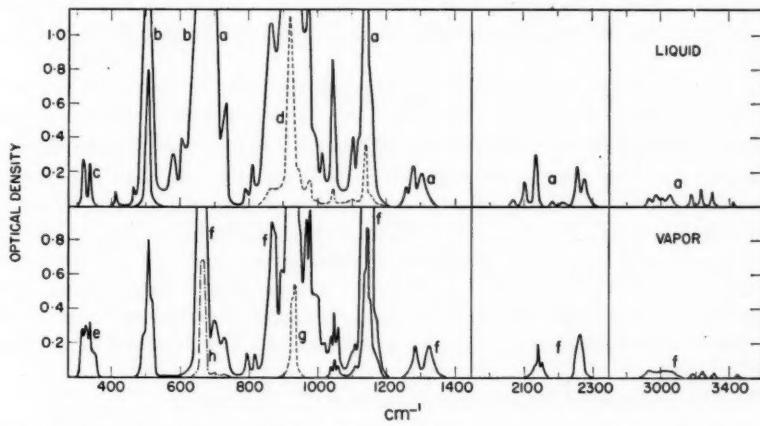


FIG. 4. The infrared spectrum of CD_3CCl_3 .
Liquid: *a*, 0.1 mm. film; *b*, 0.24 mm. film; *c*, capillary film; *d*, another capillary film.
Vapor: *e*, 6 cm. cell at 60°C ; vapor pressure $\sim 500 \text{ mm}$. *f*, 1 meter cell at 20°C ; vapor pressure $\sim 90 \text{ mm}$. *g* and *h*, 1 meter cell at 20°C . with lower pressures of vapor. Slits were $8, 4, 5, 3, 2, 3$, and 1.5 cm^{-1} in the regions $3000, 2000, 1400, 1100, 900, 700$, and 400 cm^{-1} respectively.

The theoretical product rule ratios* for both pairs of molecules have been calculated and, in Table IV, these values are compared with the observed ratios. The agreement is satisfactory.

*Dimensions for calculating moments of inertia: CH_3CN and CD_3CN ; $\text{C}-\text{H}$ and $\text{C}-\text{D} = 1.09 \text{ \AA}$, $\text{C}-\text{C} = 1.46 \text{ \AA}$, $\text{C}\equiv\text{N} = 1.16 \text{ \AA}$, angles tetrahedral. (Kessler et al. *Phys. Rev.* 79:54. 1950). CH_3CCl_3 and CD_3CCl_3 : $\text{C}-\text{H}$ and $\text{C}-\text{D} = 1.09 \text{ \AA}$, $\text{C}-\text{C} = 1.53 \text{ \AA}$, $\text{C}-\text{Cl} = 1.76 \text{ \AA}$, angles tetrahedral.

TABLE IV

TELLER-REDLICH PRODUCT RULE APPLIED TO CH₃CN AND CD₃CN AND TO
CH₃CCl₃ AND CD₃CCl₃

	Symmetry species	Observed ratio	Theoretical ratio
CH ₃ CN and CD ₃ CN	a_1	0.522	0.512
	e	0.412	0.396
CH ₃ CCl ₃ and CD ₃ CCl ₃	a_1	0.516	0.506
	e	0.375	0.371

RAMAN INTENSITIES

Crawford's (4) \sum^p rule relating the intensities of the vibrational Raman bands of isotopic molecules may be written in the form

$$[1] \quad \sum_a \frac{I_{1a}}{K_{1a} \Delta \nu_{1a}} = \sum_a \frac{I_{2a}}{K_{2a} \Delta \nu_{2a}}$$

if the conditions of irradiation and observation are the same for the isotopic molecules. Here, subscripts 1 and 2 refer to the two isotopic species; I_{1a} is the intensity of the " a "th fundamental of Raman shift $\Delta \nu_{1a}$ in isotopic molecule 1, and

$$K_{1a} = (\nu - \Delta \nu_{1a})^4 (1 - e^{-1.44 \Delta \nu_{1a}/T})^{-1}$$

where ν is 22,938 cm.⁻¹, the frequency of the exciting line, and T is the absolute temperature. The assumptions made in deriving the rule are: (a) isotopic substitution does not change the force constants of the most general quadratic potential function, (b) nor does it change the polarizability and anisotropy derivatives with respect to the internal coordinates, and, (c) anharmonicity effects may be neglected. Assumption (b) is very nearly true if there is no rotation which changes the equilibrium polarizability of the molecule in the species of vibration considered. The a_1 species of CH₃CN and CH₃CCl₃ are of this type.

Written in terms of standard intensities S (1), the rule is

$$[2] \quad \sum_a \frac{S_{1a}}{(\Delta \nu_{1a})^2} = \sum_a \frac{S_{2a}}{(\Delta \nu_{2a})^2}.$$

Although the rule was derived for the vapor phase it has been applied here to liquid phase intensities since it is expected that intermolecular interaction effects are the same for isotopic molecules.

The rule has been applied in both forms given by equations [1] and [2], and the results for the a_1 modes of CH₃CN and CD₃CN are given in Table V. There are several cases of Fermi resonance and in each case the total intensity of fundamental and overtone or combination tone was taken. Correction for overlapping of ν_2 by $\nu_5(e)$ was also necessary for CD₃CN. These bands are coincident so that the usual method of drawing symmetrical contours which is

TABLE V

	$\Delta\nu$	\bar{S}	$(\bar{S}/K\Delta\nu) \times 10^{22}$	S	$S/(\Delta\nu)^2 \times 10^7$
CH_3CN a_1 species					
ν_1	2941	0.79	16.8	4.74	5.48
	2882	0.03	0.7	0.20	0.37
ν_2	2289	0.05	1.2	0.18	0.35
	2248	0.43	10.5	1.62	3.21
ν_3	1371	0.14	4.5	0.20	1.06
ν_4	919	0.12	5.4	0.14	1.66
	Sum		39.1		12.1
CD_3CN a_1 species					
ν_1	2112	0.52	13.1	1.86	4.18
	2057	0.05	1.2	0.17	0.40
ν_2	2258*	0.75	18.1	2.58	5.06
	2209	0.14	3.5	0.43	0.87
ν_3	1103	0.05	2.1	0.06	0.47
ν_4	834	0.14	6.8	0.14	2.00
	Sum		44.8		13.0

\bar{S} is the integral intensity of the Raman band corrected for the spectral sensitivity of the phototube. The unit of the intensity scale is the intensity of the 458 cm^{-1} band of CCl_4 .

S is the standard intensity.

*Correction for overlap by ν_5 was necessary.

applicable to partially overlapping bands was inapplicable here. The assumption was made that the ratio $\bar{S}_{\nu_2}/\bar{S}_{\nu_1}$ (see Table V) was unchanged by isotopic substitution. The calculated contribution of ν_2 was subtracted from the band

TABLE VI

	$\Delta\nu$	\bar{S}	$(\bar{S}/K\Delta\nu) \times 10^{22}$	S	$S/(\Delta\nu)^2 \times 10^7$
CH_3CCl_3 a_1 species					
ν_1	2938	0.35	7.5	4.18	4.8
ν_2	1378	0.01	0.4	0.04	0.2
ν_3	1067	0.10	4.0	0.19	1.6
ν_4	521	0.61	42.4	0.74	27.3
ν_5	343*	0.25	22.4	0.13	11.5
	Sum		76.7		45.4
CD_3CCl_3 a_1 species					
ν_1	2277	0.03	0.8	0.26	0.5
	2150	0.01	0.2	0.06	0.1
	2132	0.19	4.7	1.37	3.0
	2099	0.06	1.4	0.40	0.9
	2068	0.07	1.8	0.47	1.1
ν_2	1137	0.01	0.3	0.01	0.1
ν_3	974	0.06	2.4	0.11	1.2
ν_4	503	0.70	49.8	0.81	32.2
ν_5	335	0.25	22.4	0.13	11.5
	Sum		83.8		50.6

\bar{S} and S are defined in Table V.

*Correction for overlap by ν_{11} was necessary.

at 2258 cm^{-1} in CD_3CN to leave \tilde{S}_{v_1} . Apart from being without basis, this assumption is complicated by the fact that v_1 and v_2 in CD_3CN may be in Fermi resonance. Unfortunately, v_2 makes a large contribution to the total sum and introduces a large uncertainty, probably in excess of $\pm 5\%$, to this sum. For CH_3CN conditions are more favorable, and the estimated uncertainty in the total sum is $\pm 5\%$. Within $\pm 8\%$ the sums are the same.

The results for CH_3CCl_3 and CD_3CCl_3 are presented in Table VI. One case of Fermi resonance involving v_1 in CD_3CCl_3 arises here, but a more serious uncertainty is introduced by the coincidence of v_5 and v_{11} in CH_3CCl_3 . The ratio $\tilde{S}_{v_5}/\tilde{S}_{v_{11}}$ was assumed to be the same for the two molecules ($\tilde{S}_{v_5} + \tilde{S}_{v_{11}}$ was observed to be the same and a comparison of the depolarization ratios of the three observed bands suggests that the assumption is not unreasonable). It is again unfortunate that the overlapped band makes an important contribution to the sum, but a comparison of the total sums shows that within $\pm 6\%$ they are the same.

TABLE VII
e SPECIES

CH_3CN			CD_3CN			
$\Delta\nu$	\bar{S}	S	$\Delta\nu$	\bar{S}	S	
v_5	3001	0.27	0.96	2258*	0.18	0.42
v_6	1443	0.13	0.18	1041	0.09	0.09
v_7	1047	0	0	850	0	0
v_8	379	0.23	0.06	348	0.32	0.07

\bar{S} and S are defined in Table V.

v_7 was not observed in the Raman spectra.

*Correction for overlap by v_6 was necessary.

TABLE VIII
e SPECIES

CH_3CCl_3			CD_3CCl_3			
$\Delta\nu$	\bar{S}	S	$\Delta\nu$	\bar{S}	S	
v_7	3005	0.45	3.39	2256	0.36	1.75
v_8	1444	0.17	0.44	1043	0.08	0.12
	1428					
v_9	1081	0.08	0.15	916	0.18	0.26
v_{10}	712	0.53	0.58	657	0.44	0.43
v_{11}	343*	0.30	0.11	315	0.30	0.11
v_{12}	239	0.53	0.12	231	0.51	0.11

\bar{S} and S are defined in Table V.

*Correction for overlap by v_6 was necessary.

The experimental data for the *e*-type modes of CH_3CN and CD_3CN are given in Table VII and the data for CH_3CCl_3 and CD_3CCl_3 are collected in Table VIII. Here the intensity sum rules are not expected to be valid since

molecular rotations which change the equilibrium polarizability occur. The quantities in equations [1] and [2] were however determined and are:

For CH_3CN and CD_3CN		
Equation [1]:	L.H.S. 30.2	R.H.S. 36.3
Equation [2]:	L.H.S. 5.76	R.H.S. 7.52
and for CH_3CCl_3 and CD_3CCl_3		
Equation [1]:	L.H.S. 132	R.H.S. 130
Equation [2]:	L.H.S. 49.2	R.H.S. 50.1

In each case, the deuterium substituted compound is on the right-hand side. The sum rule seems to be obeyed better for the *e*-type modes of the two methyl chloroform molecules than for the *e*-type modes of the two methyl cyanide molecules. This is probably due to the fact that the *e*-type rotational frequency changes less upon deuterium substitution in methyl chloroform than it does in methyl cyanide.

ACKNOWLEDGMENTS

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THE EFFECT OF ADDITION AGENTS ON CATHODE POLARIZATION DURING ELECTRODEPOSITION OF COPPER AT SINGLE CRYSTAL COPPER CATHODES¹

BY K. EKLER² AND C. A. WINKLER

ABSTRACT

The polarization-time relations for the initial (P_i), maximum (P_{\max}), and pseudo-steady-state (P_s) polarizations on copper single crystals in the absence and presence of gelatin and gelatin plus chloride ion were found to depend upon crystal orientation. The P_i and P_{\max} in the absence of gelatin, the P_i in its presence, and the static potentials were all similarly related to the reticular density. The P_i increased, and the time to maximum polarization (t_{\max}) decreased, with increase of current density; the relations between these quantities showed marked differences for the different crystals. The variation with reticular density of P_i and P_{\max} in the absence of addition agents and of P_i in its presence probably represents differences in activation overpotential at the various crystal faces. The adsorption of gelatin on different crystal faces was also found to be markedly different. Polarization in the presence of gelatin was decreased by small amounts of chloride ion; a linear relation for all the crystals used was obtained by plotting the increase in polarization caused by gelatin against the decrease caused by 2 mgm./liter chloride ion in the presence of gelatin. In the absence of addition agent, change of acid concentration from 50 to 200 gm./liter had no effect on P_i and addition of chloride ion had no effect on P_s at single crystal cathodes.

INTRODUCTION

A number of papers from this laboratory have discussed the changes in cathode polarization at polycrystalline cathodes during electrodeposition of copper from acid copper sulphate electrolyte containing addition agents. Since the earliest of these studies (4), it has been of interest to examine the behavior with single crystal copper cathodes under similar conditions. Ample evidence exists that significantly different lattice energies are associated with different crystal faces of a single crystal, and such differences might be expected to influence not only the adsorption of an addition agent, hence the polarization in its presence, but perhaps also the polarization values in the absence of addition agent. The present paper represents a re-examination with single crystal cathodes of the more prominent features found previously to characterize the polarization behavior with polycrystalline cathodes.

EXPERIMENTAL AND RESULTS

Crystals 1½ in. × ½ in. × ¼ in. were purchased from Horizons Inc., Cleveland, Ohio. Their orientations were specified to be (111), (100), (110), (211), (410), and (322), referred to the longitudinal axis.

The interplanar spacings shown in Table I were calculated from the relation (3):

$$d = s/\sqrt{(h^2 + k^2 + l^2)}$$

where h , k , and l are the Miller indices and s is a term which for a face centered

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cubic lattice, e.g. copper, is equal to 0.5 if one or two indices are odd; otherwise it is unity.

It should be noted that although two lattice planes of different Miller indices may have the same interplanar distances, e.g. (410) and (322), hence the same reticular densities (2), examination of a space lattice model readily revealed that the environment of a given atom in the two cases is quite different.

The polarization measurements were made in a modified Haring cell as described previously (4).

Prior to every experiment after the first one with a given crystal, deposited copper was carefully removed with a succession of files of decreasing roughness. A special guide was designed to ensure uniform removal of the deposit and thus preserve the original orientation of the crystal face. A rectangular groove was milled along a 10 in. brass bar to accommodate interchangeable files, while the crystal to be ground was placed in a slot milled into a brass block 2 in. long. When the block was inverted over the bar, and allowed to slide on it, the deposit of copper was removed while retaining parallelism of the crystal faces as indicated by micrometer measurements. The crystal was ground finally on metallographic papers 0 to 4/0 after which it was transferred to a suitable holder and all of the crystal surface coated with paraffin wax except the face under examination. The dimensions of the exposed area were determined with a table cathetometer so that the current could be adjusted to the desired apparent current density for the next operation of electropolishing. Chemical etching did not allow reproducible polarization values to be obtained.

The electropolishing bath consisted of 42.5% orthophosphoric acid (6). To minimize gassing, a copper cathode of area approximately 20 times that of the crystal was used. The potential between the electrodes was 4 volts and the spacing approximately three and one-half inches. The crystal was anodically polished for eight minutes at a starting current density of 12 amp./dm². An increase of polishing time to 20 min. gave identical results. Pitting of the surface was largely avoided by dislodging gas-bubbles as soon as their formation was detected.

After it had been electropolished, the crystal was rinsed with distilled water and immediately placed in a Haring cell containing electrolyte in presence of air at $25 \pm 0.1^\circ\text{C}$. Unless otherwise stated the electrolyte contained 125 gm./liter Merck's reagent grade copper sulphate pentahydrate and 100 gm./liter Baker's C.P. sulphuric acid in freshly distilled water. It was not stirred during polarization measurements.

Potentials were measured with a recording potentiometer (Brush Development Co., Cleveland, Ohio, Recorder BL 201, DC-Amplifier BL 932) and a potentiometer (Tinsley, Type 3184 D).

A reproducibility within ± 5 millivolts was required and generally obtained without difficulty.

For all experiments in the absence of addition agents the cathode was allowed to remain in contact with the electrolyte for 10 min. before starting

electrolysis. An increase of this immersion time to 30 min. gave identical polarization values. When addition agent was present in the electrolyte the immersion time was 15 min. An increase from 15 to 120 min. did not show any detectable polarization changes.

(i) *No Addition Agent Present*

The polarization-time relations for the various crystals at 2 amp./dm.² are shown in Fig. 1. From the original tracings of these curves on the recording

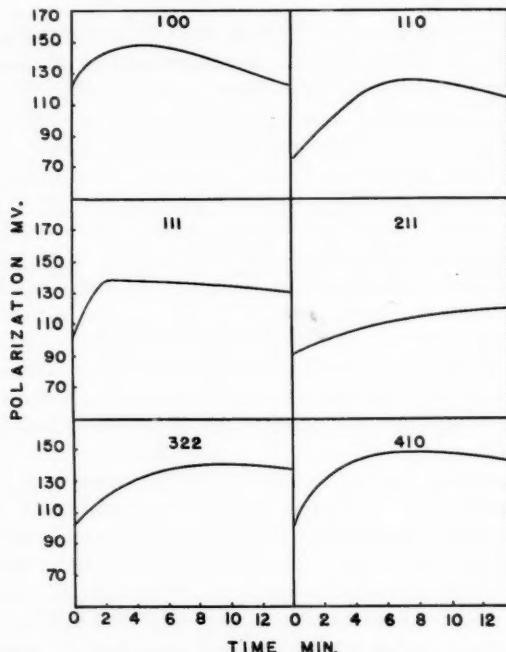


FIG. 1. Polarization-time relations at single crystal cathodes.

potentiometer, values of the initial (P_i) and maximum (P_{\max}) polarization respectively were obtained and are recorded for the six crystals in Table I.*

The relative static potentials of the crystals are also shown in the table. To obtain these values, each crystal was immersed in the standard electrolyte in the presence of air and the electrode potential measured relative to a capillary probe filled with the same electrolyte in contact with a calomel half-cell through a closed, ungreased stopcock. Potential measurements were taken every five minutes until a steady state was obtained after 70 to 120 min.

The initial polarization and times required to attain the maximum polarization values for current densities from 0.2 to 4.0 amp./dm.² are summarized

*While various quantities may be graphically represented in relation to the d -values, it should be noted that d is not a "running parameter", hence such plots are of doubtful significance.

TABLE I

INITIAL (P_i) AND MAXIMUM (P_{\max}) POLARIZATION VALUES, AND STATIC POTENTIALS, AT SINGLE CRYSTAL CATHODES IN THE ABSENCE OF ADDITION AGENT

Crystal (Miller indices)	Interplanar distance (d)* (Å)	P_i (mv.)	P_{\max} (mv.)	Static potential (mv.)
(111)	0.5774	102	132	84
(100)	0.5000	120	148	90
(110)	0.3536	78	123	83
(211)	0.2041	90	118	69
(410)	0.1213	99	140	77
(322)	0.1213	101	147	80

*Referred to edge of unit cube.

in Fig. 2. (For clarity the curves for only four crystals are shown; the other two are similar.) The latter quantity for a given crystal shifted systematically to lower values as the current density was increased.

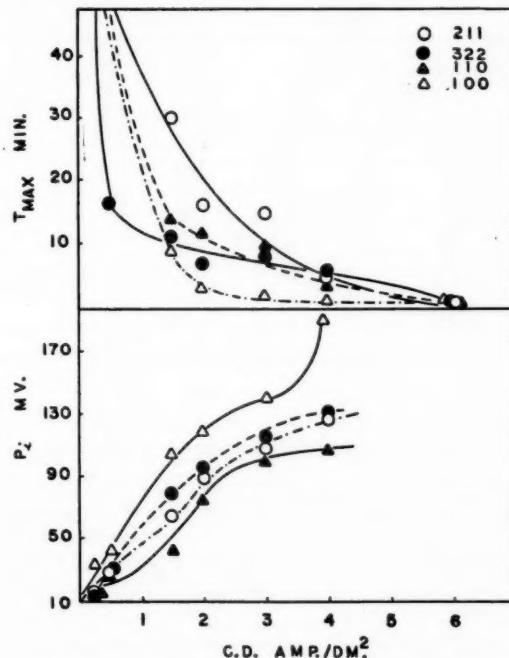


FIG. 2. Variation with current density of initial polarization (P_i) and time to maximum polarization (t_{\max}).

The concentration polarization for the (100) face at 2 amp./dm.² was determined with an oscilloscope (11) (Dumont 304H) and was found to be 17 ± 2 mv. This is comparable with the value (20 mv.) observed for polycrystalline copper under similar conditions.

An attempt was made to study perpetuation of the base structure at 0.5 and 0.2 amp./dm.². The deposition was interrupted after 10 min. and the polarization allowed to dissipate. The current was then turned on again and the second recorded pattern compared with the original. It was noted that at 0.5 amp./dm.² only the (111) face seemed to repeat the original pattern; all the other crystals gave somewhat higher initial polarization values in the second pattern. At 0.2 amp./dm.² the values of the initial pattern appeared to be repeated in the second pattern only with the (111) and (410) crystal faces.

At 2 amp./dm.² microscopic examination of the deposits showed islands of varying reflectivity, indicative of polycrystallinity after deposition times of three minutes or less.

Change of the sulphuric acid concentration of the electrolyte from 50 to 200 gm./liter resulted in no pronounced or systematic changes of polarization, as indicated by the following values:

Acid conc. (gm./l.)	Polarization values for crystal faces					
	(110)		(111)		(410)	
	P_i	P_{\max}	P_i	P_{\max}	P_i	P_{\max}
50	75	111	105	116	102	140
100	78	118	102	130	101	146
200	67	105	99	120	91	124

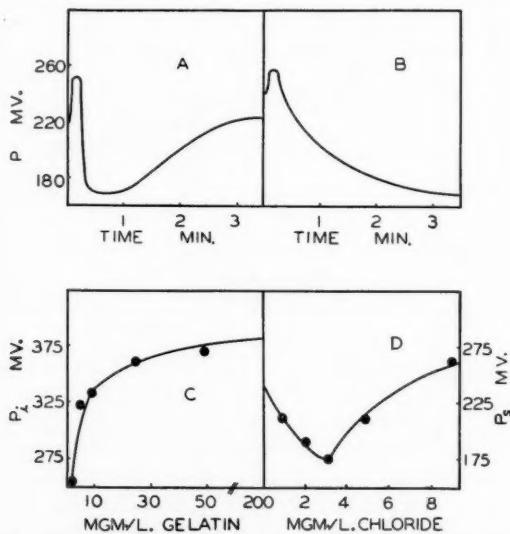


FIG. 3. A: Polarization-time relation at a single crystal cathode in the presence of gelatin. B: Polarization-time relation at a single crystal cathode in the presence of gelatin and chloride.

C: Relation between initial polarization at a single crystal cathode and gelatin content of the electrolyte.

D: Relation between steady-state polarization at a single crystal cathode and chloride content of the electrolyte in the presence of gelatin.

(ii) *Addition Agent Present*

An experiment in the presence of addition agent was usually made following an experiment in the standard electrolyte, after removing the previous copper deposit and preparing the crystal anew by electropolishing.

In the presence of gelatin (25 mgm./liter), the single crystal cathodes gave polarization-time curves similar to those observed previously (9) with polycrystalline cathodes (Fig. 3A). The initial polarizations (P_i) for the six crystals varied from 265 to 365 mv., while the steady-state polarization (P_s)* showed a variation with orientation ranging from 200 to 270 mv. The curve relating initial polarization (P_i) to gelatin concentration was similar in shape for the six crystals (Brush oscilloscope). Typical of the behavior is the plot shown in Fig. 3C, for the (100) crystal. However the polarization values for a given amount of gelatin differed for the different crystal faces, as shown in Table II.

TABLE II
RELATION BETWEEN INITIAL POLARIZATION AND GELATIN CONTENT OF THE ELECTROLYTE

Gelatin conc. (mgm./l.)	Initial polarization (mv.)					
	(111)	(100)	(110)	(211)	(322)	(410)
0	105	120	75	90	101	102
2	164	205	178	207	190	255
5	222	325	220	230	240	280
10	254	335	260	266	274	290
25	271	365	265	274	290	350
50	284	370	287	292	296	356
200	304	387	290	300	307	366
Adsorption (%) from electrolyte containing 1.5 mgm./l. gelatin	18	38	7	7	25	21
Interplanar spacing (d -value)	0.5774	0.5000	0.3536	0.2041	0.1213	0.1213

It is interesting to note that P_i changes with interplanar spacing in a similar manner for all the systems, including that which contained no gelatin.

The dependence of P_i on d -value in the presence of gelatin prompted an attempt to determine the relative extents of adsorption of gelatin on the six crystals. A calibration curve was first established, to relate P_s measured at a polycrystalline cathode (which had been given a steady-state surface) to the gelatin concentration in the electrolyte (up to 2 mgm./liter). Electrolyte containing 1.5 mgm./liter gelatin and a polycrystalline cathode with a steady-state surface were then placed in the Haring cell and the single crystal of copper, with known area exposed, was immersed during one hour with constant agitation but no passage of current, to permit adsorption of gelatin on the crystal. The crystal and stirrer were then removed from the cell and the value of P_s in the gelatin-depleted electrolyte determined. The corresponding gelatin

*This really corresponds only to a pseudo steady state for the short deposition times involved. Had deposition been continued for a sufficiently long time, it is probable that the true steady-state values would all have been similar at the eventual polycrystalline surfaces.

concentration remaining in the electrolyte could then be obtained from the calibration curve, and the extent of adsorption of gelatin calculated. Adsorption of gelatin on the cell walls and polycrystalline cathode was eliminated as a factor by allowing the cell to stand with the appropriate electrolyte for 10 min. before each experiment, after which fresh electrolyte was introduced. All conditions used in establishing the calibration curve were reproduced as precisely as possible in the adsorption experiments; the only difference was immersion of the single crystal in the latter. The procedure gave values for adsorption on a given crystal that were reproducible within $\pm 4\%$. The relative extents of adsorption at the different crystal surfaces are shown in Table II. It will be noted that the variation of per cent adsorption with d -value parallels rather closely corresponding changes in P_s .

When chloride (2 mgm./liter) was added to the electrolyte in the absence of gelatin the polarization behavior was substantially the same as that in the standard electrolyte. This was true for immersion times of 1 to 30 min. With polycrystalline cathodes the addition of chloride to the electrolyte had little effect with the immersion time of one minute but caused about 15 mv. increase in polarization when the immersion time was increased to 30 min.

The results reported so far were obtained on the six crystals of known orientation. A second group of crystals available in this investigation consisted of 25 crystals, each 3 in. $\times \frac{1}{4}$ in. $\times \frac{1}{4}$ in., grown from melts of spectroscopically pure copper without benefit of seed crystal.* As a consequence the Miller indices of most of these crystals were quite complex and not suitable for estimation of interplanar distances.

With these single crystals, as with the ones previously used, the addition of chloride (2 mgm./liter) to electrolyte containing gelatin (25 mgm./liter) had a pronounced effect on P_s , though not on P_{\max} (cf. Figs. 3A and 3B as typical). There appeared to be no significant effect of immersion time (up to 120 min.) on P_{\max} or P_s in such systems. Experiments with two of the single crystals showed that the relation between P_s and chloride concentration (Fig. 3D) in the presence of gelatin (25 mgm./liter) was similar to that observed with polycrystalline cathodes.

When all the available data† for the various crystals were considered, it was found that the decrease in P_s caused by the chloride in the presence of gelatin ($-\Delta P_{Cl}$) was correlated with the increase in P_s caused by the gelatin alone (ΔP_{gel}) (Fig. 4A; line drawn by least squares).

In the above experiments, a given amount of chloride appeared capable of nullifying polarization increments which differed because of different cathode surfaces. This suggested that a similar study be made in which the polarization increments at a given cathode face were varied by addition of different amounts of gelatin. For this purpose, steady-state polycrystalline cathodes were used (5) and the behavior was examined not only with a constant amount of chloride (2 mgm./liter) (broken line, Fig. 4B) but with the amount of chloride deter-

*We are indebted to Mr. C. Cupp, Department of Metallurgy, University of Toronto, for preparing these crystals and determining their orientations.

†With most of the crystals data were obtained for two orientations corresponding to two faces of the crystal at right angles.

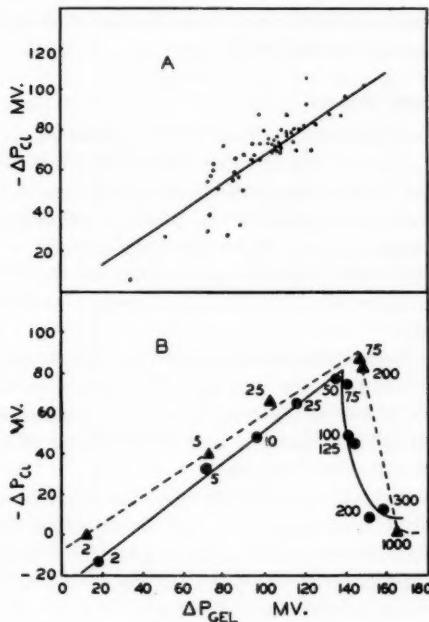


FIG. 4. Relation between decrease ($-\Delta P_{Cl}$) in steady-state polarization caused by chloride in the presence of gelatin and the increase (ΔP_{Gel}) in steady-state polarization caused by gelatin alone.

Top: Single crystal cathodes, with 25 mgm./liter gelatin, 2 mgm./liter chloride.

Bottom: Polycrystalline cathodes with amounts of gelatin (mgm./liter) shown on figure.

mined experimentally (8) that gave the minimum polarization for each gelatin concentration (full line, Fig. 4B).

When the effect of chloride (2 mgm./liter) in the presence of gelatin (25 mgm./liter) was examined for the six crystals of known orientation, the values of $-\Delta P_{Cl}$ were found to relate in much the same way as P_i to the d -values for these crystals.

DISCUSSION

The results of the present study in the absence and presence of addition agents demonstrate rather marked differences in behavior of the cathode polarization with the changes in crystal orientations and changes from single- to poly-crystallinity. A polycrystalline metal surface consists of an array of crystal faces of diverse orientations, edges, corners, and boundaries. Each type of orientation has its characteristic arrangement of atoms which influences the surface free energy of the crystal face. The properties of the polycrystalline surface therefore depend upon the properties of these individual parts. In some cases, e.g. cold rolled metal, there may be a preponderance of certain

preferred orientations and the properties of the surface therefore may be weighted in one direction or the other.

(i) *No Addition Agent Present*

The initial polarization on electropolished *polycrystalline* copper, in the absence of addition agent, lies between the values for single crystals; this is reasonable because of the composite nature of the former. The value, 85 mv., is biased towards the lower values for the crystals investigated. This might be attributed to a preponderance of certain orientations on the rolled polycrystalline copper cathodes. The static potential for the polycrystalline cathode, 73.7 mv., is similarly related to the static potentials of the crystals, probably for a like reason.

The maxima observed in the polarization-time relations for the six crystals of specified orientations indicate that opposing processes are involved in the polarization changes. It seems reasonable that these processes might be:

- (a) Increase of total polarization due to build-up of concentration and hydrogen-ion interference polarizations.
- (b) Increase of polarization due to deposition of nuclei of orientations different from that of the base crystal, such that discharge of atoms requires a higher activation polarization than on the original base matrix.
- (c) Decrease of total polarization due to increase of true surface area of the cathode, hence decrease of true current density.

The pseudo-steady-state value might be expected when the single crystal base eventually becomes overgrown with nuclei of diverse orientations to such an extent that the increase of true surface area, with the attendant decrease of true current density, hence of polarization, finally predominates.

As expected, t_{\max} decreased systematically with an increase in current density, owing in all probability to increased rate of nucleation with consequent increase in rate of surface roughening.

The values of the initial polarization, i.e. in the absence of significant concentration polarization, must contain an activation overpotential and presumably also an ohmic component due to hydrogen ion interference. In the present study, no effect of increased acid concentration on this initial polarization at three different crystal cathodes was observed in the range of 50 to 200 mgm./liter acid. On the other hand, with polycrystalline cathodes, a linear increase of polarization with acid concentration was previously observed in this laboratory (10). The extent of the increase was the same in the absence and presence of addition agent (cystine), and the opinion was expressed that adsorption of hydrogen ion was probably not involved. However, there seems no alternative to assuming optimal adsorption of hydrogen ion on the single crystal cathodes over the range of acid concentrations studied, to account for the absence of an acid effect with these cathodes. The behavior with polycrystalline cathodes might then be ascribed to an adsorption which is less than optimal, if it is further assumed that the adsorption-concentration relations for hydrogen ion and cystine are comparable in the ranges of concentrations concerned.

If, as seems reasonable, the contribution to the polarization at single crystal cathodes due to hydrogen ion is comparable with or less than that at polycrystalline cathodes (30), the *differences* in the hydrogen ion effect at the different single crystals would be less, probably much less than 30 mv., and the observed differences in P_i may be taken to reflect mainly differences in activation overpotentials at different crystal faces.

The differences in P_{\max} might also be due largely to differences in activation overvoltage for the different crystal orientations, but it must be remembered that by the time P_{\max} occurs, the single crystal surface might have undergone considerable change due to the formation of nuclei with orientations other than that of the crystal base.

The variation of P_i and P_{\max} with d -value for the crystal might reasonably be expected to reflect changes in the surface free energy, which in turn should presumably be associated with the different static potentials of the crystals. In general, the P_i and P_{\max} values appear to be related to the reticular density in much the same way as the static potentials. However, there is not a linear relation between either P_i or P_{\max} and the static potentials when all the data are considered. It would appear therefore that polarization is not determined solely by the surface lattice energy. It is interesting to note, however, that the plot of P_i -values against static potentials may be considered to yield a roughly linear relation for five of the six crystals used; the P_i value for the (110) face only seems to deviate to an unacceptable extent from the relation. For the dynamic conditions that prevail in polarization measurements, it seems likely that the spatial distribution and density of atoms in the lattice may play a part which is not reflected in the contribution of these factors to a thermodynamic quantity such as the static potential.

(ii) Addition Agent Present

A satisfactory explanation of the P_i -time pattern observed in the presence of gelatin seems to be possible along the lines suggested by Parsons and Winkler (9). The rise in polarization to the early maximum is readily explained by cataphoretic migration of cuprous-gelatin complexes to the cathode when the circuit is completed, thus increasing the amount of addition agent on the cathode with consequent increase of polarization. Simultaneously, slight depletion of the gelatin in the immediate neighborhood of the cathode must occur. When deposition is initiated, new copper surface is laid down (either with growth of the existing crystal or as new nuclei) in an environment of electrolyte partially depleted of gelatin, such that adsorption of gelatin on the newly formed surface is hindered and the true current density decreases with increase in extent of cathode area free from addition agent. The polarization therefore tends to decrease again, and a maximum is observed in the polarization-time curve. Eventually, of course, the supply of gelatin at the cathode face is replenished by convection and the polarization passes through a minimum to a steady-state value. The effect of immersion time on the polarization pattern with polycrystalline electrodes was attributed to corrosion which would serve to expose different crystal faces and change the true surface area until

a steady state was reached. The absence of any effect of immersion time when single crystals were used may reasonably be attributed to the absence of such change in true surface area due to corrosion.

The value of P_i in the presence of gelatin consists probably of an activation overpotential, an ohmic component due to adsorbed cuprous-gelatin complexes, and possibly some component due to hydrogen ion interference. The observation that the presence of gelatin makes no substantial change in the relation between d -value and P_i suggests that the activation overpotential in the presence and absence of gelatin is the same, and corresponds to the deposition of aquo-complexes in both cases, while the ohmic and hydrogen ion components of the polarization are practically constant for the different crystals. This latter condition, in turn, would probably prevail if all the crystals were almost completely covered by adsorbed cuprous-gelatin complexes.

The effect of chloride ion in reducing the polarization is readily explained by assuming that the chloride ion acts as an electron bridge as suggested by Heyrovsky (7). Consideration of Fig. 4B indicates that a limit is reached, perhaps when the cathode becomes so heavily overlaid with adsorbed complexes that access of the chloride ion to effective positions is virtually precluded. This view would gain support from the polarization - gelatin concentration curve, from which it would appear that a plateau, presumably corresponding to essentially complete coverage of the cathode by gelatin or its copper complexes, occurs in the neighborhood of 75 mgm./liter gelatin.

In the presence of gelatin plus 2 mgm./liter chloride the polarization gradually decreased from P_i to P_s with no minimum in the polarization-time curve. This behavior seems reasonable enough since, after the maximum is passed and new surface is laid down in the presence of chloride ion, any tendency for polarization to increase again because of adsorption of complexes should be offset by the facilitated electron transfer effected by the chloride ion. Hence, as deposition continues and the polycrystalline character of the cathode surface is increased, the polarization should merely decrease to that corresponding to deposition on a polycrystalline surface in the presence of gelatin plus chloride.

With single crystals, 2 mgm./liter chloride ion (no gelatin present) had no effect on the pseudo-steady-state polarization, whereas with polycrystalline cathodes the steady-state polarization was increased about 15 mv. (8). Adamek has suggested that this increase be associated with migration of atoms into lattice positions following their deposition in out-of-lattice positions in the presence of chloride by the dismutation reaction (1)



Failure to observe the increase with single crystals might be expected on this basis, since deposition on the single crystals until the pseudo steady state was established presumably consisted largely of nucleus formation, with limited crystal growth, and dismutation could occur freely on the crystal face without subsequent migration of atoms into an established lattice.

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THE TERTIARYBUTYLBENZENES

III. THE SYNTHESIS OF 2,4,6-TRI-*t*-BUTYLBENZOIC ACID AND THE DISSOCIATION OF DI- AND TRI-*t*-BUTYLBENZOIC ACIDS¹

BY EILEEN E. BETTS² AND L. ROSS C. BARCLAY

ABSTRACT

2,4,6-Tri-*t*-butylbromobenzene, m.p. 177–177.5°, was prepared by the bromination of 1,3,5-tri-*t*-butylbenzene in the presence of silver nitrate. The reaction of 2,4,6-tri-*t*-butylbromobenzene and *n*-butyllithium gave 2,4,6-tri-*t*-butylphenyllithium, which on carbonation yielded 2,4,6-tri-*t*-butylbenzoic acid, m.p. 297°. A solution of this acid in fuming sulphuric acid yielded a methyl ester, m.p. 96–98°, when it was poured into absolute methanol. Similar treatment of 1,4-di-*t*-butylbenzene with bromine gave 2,5-di-*t*-butylbromobenzene, which on reaction with *n*-butyllithium and subsequent carbonation gave 2,5-di-*t*-butylbenzoic acid. The reaction of 1,3,5-tri-*t*-butylbenzene with acetyl chloride in the presence of aluminum chloride gave a liquid ketone, and hypohalide oxidation of this ketone yielded 3,5-tri-*t*-butylbenzoic acid. The ultraviolet absorption spectra of the two bromo compounds and the three acids were measured and are discussed. The considerable acid-weakening effect in 2,4,6-tri-*t*-butylbenzoic acid is attributed to steric hindrance to the formation of the carboxylate anion.

We have been interested in the synthesis of derivatives of 1,3,5-tri-*t*-butylbenzene required in a study of the influence of two bulky ortho *t*-butyl groups on aromatic functional groups. The present communication describes the synthesis of 2,4,6-tri-*t*-butylbenzoic acid. As a preliminary study of steric hindrance in such a structure, the ultraviolet spectrum and apparent dissociation constant of this acid are measured and compared with those of 3,5-di-*t*-butyl- and 2,5-di-*t*-butylbenzoic acids.

1,3,5-Tri-*t*-butylbenzene, prepared by the alkylation of 1,4-di-*t*-butylbenzene with *t*-butyl chloride (1), was brominated with bromine in the presence of silver nitrate by a procedure similar to the one used by Derbyshire and Waters (7) for the bromination of chloro- and bromo-benzenes. The 2,4,6-tri-*t*-butylbromobenzene prepared by this method was identical with 2,4,6-tri-*t*-butylbromobenzene prepared by the Sandmeyer reaction on 2,4,6-tri-*t*-butylaniline. Attempts to react 2,4,6-tri-*t*-butylbromobenzene with magnesium were unsuccessful.

2,5-Di-*t*-butylbromobenzene was prepared by the addition of bromine to 1,4-di-*t*-butylbenzene in the presence of silver nitrate. The procedure of Thiec (15) was used to prepare 2,5-di-*t*-butylbenzoic acid from 2,5-di-*t*-butylbromobenzene by refluxing with *n*-butyllithium and carbonation of the resulting 2,5-di-*t*-butylphenyllithium. Similar treatment of 2,4,6-tri-*t*-butylbromobenzene with *n*-butyllithium gave 2,4,6-tri-*t*-butylphenyllithium, which on hydrolysis gave 1,3,5-tri-*t*-butylbenzene or on carbonation gave 2,4,6-tri-*t*-butylbenzoic acid, m.p. 297°. The methyl ester, m.p. 96–98°, of 2,4,6-tri-*t*-butylbenzoic acid was prepared from the acid by the procedure of Newman (11).

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The reaction of 1,3,5-tri-*t*-butylbenzene with acetyl chloride in the presence of aluminum chloride for two hours at room temperature gave a brown liquid ketone, 3,5-di-*t*-butylacetophenone, whose 2,4-dinitrophenylhydrazone melted at 212–214°. Hypohalide oxidation of this ketone gave an acid, 3,5-di-*t*-butylbenzoic acid, m.p. 173–174°. Carpenter and Easter (6) report 3,5-di-*t*-butylbenzoic acid, m.p. 169.5–170.5°, by oxidation of a hydrocarbon described as 3,4-di-*t*-butyltoluene by Capeller (5), but given the 1,3,5 configuration by Schlatter (14). No conclusive evidence has been given for the structure of this acid. Brown (4) has shown that inherent strain in an *o*-di-*t*-butyl configuration makes the existence of such a structure highly improbable. On this basis, and from comparison of the absorption spectrum and ionization constant with those of 2,5-di-*t*-butylbenzoic acid, we have assigned the structure 3,5-di-*t*-butylbenzoic acid. This product requires a replacement of a *t*-butyl group by an acetyl group during the Friedel-Crafts acetylation of 1,3,5-tri-*t*-butylbenzene. This result is analogous to the anomalous acetylations obtained by Nightingale and Hucker (12) where *p*-di-*t*-butylbenzene yielded *p*-*t*-butylacetophenone.

The ultraviolet absorption spectra of 2,4,6-tri-*t*-butylbromobenzene and 2,5-di-*t*-butylbromobenzene (Fig. 1), and of 2,4,6-tri-*t*-butylbenzoic, 2,5-di-*t*-butylbenzoic, and 3,5-di-*t*-butylbenzoic acids (Fig. 2) were measured in cyclohexane with a Beckman DU spectrophotometer. In Fig. 1, 2,5-di-*t*-butyl-

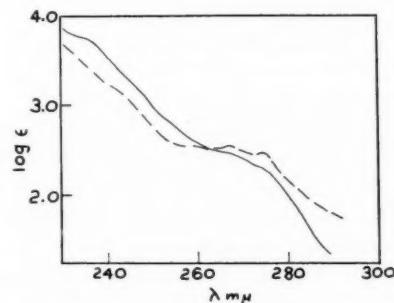


FIG. 1. Ultraviolet spectra in cyclohexane:
— 2,5-di-*t*-butylbromobenzene
(b.p. 150° (12–13 mm.));
— 2,4,6-tri-*t*-butylbromobenzene
(m.p. 177–177.5°).

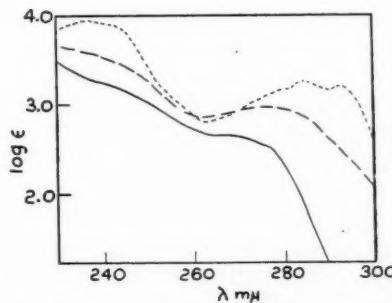


FIG. 2. Ultraviolet spectra in cyclohexane:
— 2,4,6-tri-*t*-butylbenzoic acid
(m.p. 297°);
— 2,5-di-*t*-butylbenzoic acid
(m.p. 128°);
- - - 3,5-di-*t*-butylbenzoic acid
(m.p. 173–174°).

bromobenzene shows slight absorption at 2750 and 2670 Å, while 2,4,6-tri-*t*-butylbromobenzene has no bands. The presence of the second *t*-butyl group ortho to the bromine in 2,4,6-tri-*t*-butylbromobenzene evidently blots out resonance interaction between the bromine and the benzene ring. A similar effect of the bulky *t*-butyl groups is more noticeable in the spectra of the *t*-butylbenzoic acids (Fig. 2). In the case of the di-*t*-butylbenzoic acids a shift of

a *t*-butyl group from a meta position, as in 3,5-di-*t*-butylbenzoic acid, to a position ortho to the carboxyl group removes the K-band near 2360 Å. In addition, the benzenoid "fine structure" absorption of 3,5-di-*t*-butylbenzoic acid (2800–2950 Å) is replaced by weaker general absorption at 2700 Å. When two *o*-*t*-butyl groups are present this effect is very pronounced—so much so that 2,4,6-tri-*t*-butylbenzoic acid has no characteristic absorption maxima, only rising absorption towards shorter wave lengths.

The relative dissociation constants of benzoic, 2,5-di-*t*-butylbenzoic, 3,5-di-*t*-butylbenzoic, and 2,4,6-tri-*t*-butylbenzoic acids (Table I) were measured by potentiometric titration in 50% methanol-water using a Beckman pH meter, with a glass electrode and a calomel reference electrode. The results for benzoic acid agree well with that of pK_a 5.15 obtained by Bright and Briscoe (3) but not with the value of 5.62 recently obtained by Hammond and Hogle (9). Other workers (8) have used aqueous dioxane media. Although our procedure yielded reliable comparative pK_a values the necessity for some standard technique is apparent.

TABLE I

Acid	pK_a		
	($\frac{1}{4}$ point)	($\frac{1}{2}$ point)	($\frac{3}{4}$ point)
Benzoic	5.19	5.21	5.20
2,5-Di- <i>t</i> -butylbenzoic	5.03	5.05	5.05
3,5-Di- <i>t</i> -butylbenzoic	5.78	5.80	5.84
2,4,6-Tri- <i>t</i> -butylbenzoic		6.25	

A number of effects can be brought into play in the steric effect of ortho-substituted benzene derivatives. These effects have been discussed by Ingold (10) and recently summarized by Hammond and Hogle (9). Ingold explains that aromatic conjugation weakens a benzoic acid and that the often-observed acid-strengthening effect in *o*-substituted benzoic acids is due to a twisting of the carboxyl group from the plane of the benzene ring. In the case of 2,5-di-*t*-butylbenzoic acid this acid-strengthening effect is greater than the hindering effect of one *t*-butyl group to the formation of the anion and the acid-weakening effect of electron-repelling *t*-butyl groups. The latter effect is important in 3,5-di-*t*-butylbenzoic acid where there is a considerable rise in the pK_a value. 2,4,6-Tri-*t*-butylbenzoic acid is a much weaker acid than benzoic. We attribute this to the controlling hindering effect of two *o*-*t*-butyl groups which decrease the stability of the carboxylate ion.

EXPERIMENTAL³*2,4,6-Tri-*t*-butylbromobenzene*(a) *By Direct Bromination*

1,3,5-Tri-*t*-butylbenzene, m.p. 74° (2.46 gm., 0.01 mole), was dissolved in

³Melting points are uncorrected.

30 ml. of glacial acetic acid in a 100 ml. round-bottom flask. To this solution was added 0.60 ml. (a slight excess of 0.01 mole) of bromine, solutions of 5 ml. of concentrated nitric acid in 10 ml. of water and of 1.7 gm. of silver nitrate in 5 ml. of water, the addition of the last solution taking one half-hour. Another 20 ml. of glacial acetic acid was added and the reaction mixture heated on the steam cone for an hour with occasional shaking, a loose cork being placed in the mouth of the flask to prevent excess escape of bromine. At the end of the hour most of the bromine color had disappeared and the oil which had appeared on the solution when it was first heated had solidified. The hot reaction mixture was poured into 200 ml. of water, a little sodium sulphite added to destroy excess bromine, and then 5% sodium hydroxide until the solution was approximately neutral. The cooled solution was extracted three times with ether, the ether extracts washed with water, and most of the ether removed by distillation. The yellow solid, which separated from the residue on cooling, was collected on a filter paper, water was added to the filtrate and more product was collected (total yield 1.7 gm., 50%). After four recrystallizations from ethanol, the shining white plates melted at 177-177.5°. In a subsequent bromination the yield was 67%. Anal. Found: C, 66.52, 66.57; H, 9.09, 8.86; Br, 24.51, 24.40. Calc. for $C_{18}H_{29}Br$: C, 66.46; H, 8.98; Br, 24.57.

(b) *By the Sandmeyer Reaction*

1,3,5-Tri-*t*-butylbenzene was nitrated by the addition of 6.1 gm. of fuming nitric acid (sp. gr. 1.5) to 22 gm. of the hydrocarbon dissolved in a solution of 30.5 ml. of acetic acid and 23.6 ml. of acetic anhydride. The yellow precipitate, 2,4,6-tri-*t*-butylnitrobenzene, which was isolated 45 min. later by filtration, melted at 204-206° after recrystallization from petroleum ether (yield 80%).

2,4,6-Tri-*t*-butylaniline, m.p. 146-148°, was prepared by the reduction of 2,4,6-tri-*t*-butylnitrobenzene using the procedure of Bartlett and co-workers (2).

Three grams of 2,4,6-tri-*t*-butylaniline was added to 30 ml. of glacial acetic acid, 15 gm. of 48% hydrobromic acid was then added, the suspension warmed until solution was complete and then cooled with stirring to 0°. The slow addition of a solution of 1.5 gm. of sodium nitrite in 7.5 ml. of water caused the formation of a yellow precipitate. This was added to a solution of 5 gm. of cuprous bromide in 30 gm. of 48% hydrobromic acid. After it was left for two hours at room temperature, the purple reaction mixture was heated on the steam cone for 30 min., cooled, water added until the reaction mixture was yellow, then concentrated hydrochloric acid until it was clear. The organic layer, which was a semisolid mass on the bottom of the flask, was removed, washed with water, and placed on a filter paper. A yellow oil was drawn off with suction, leaving colorless needles, m.p. 100-176° (wt. 0.370 gm.). After two recrystallizations from ethanol the reaction product, in the form of shining plates, melted at 177.5-178° and did not depress the melting point of the 2,4,6-tri-*t*-butylbromobenzene prepared by direct bromination. The ultraviolet absorption spectra of the two samples were identical.

Attempts to react 2,4,6-tri-*t*-butylbromobenzene with magnesium or sodium in absolute ether failed.

*2,5-Di-*t*-butylbromobenzene*

2,5-Di-*t*-butylbromobenzene was prepared by the addition of bromine to 5.7 gm. (0.03 moles) of 1,4-di-*t*-butylbenzene using the same procedure as for the direct bromination of 1,3,5-tri-*t*-butylbenzene. The reaction mixture was heated for eight hours on the steam cone and the product was distilled *in vacuo* to give 1.7 gm. (21% yield) of 2,5-di-*t*-butylbromobenzene, a yellow liquid (b.p. 150° at 12–13 mm.).

*2,5-Di-*t*-butylbenzoic Acid*

An approximately 0.1 molar *n*-butyllithium solution was prepared by the procedure given in *Organic Reactions* (13).

2,5-Di-*t*-butylbromobenzene (1 gm.), 5 ml. of the *n*-butyllithium solution, and 10 ml. of absolute ether were refluxed in an atmosphere of dry nitrogen for 40 min. Dry carbon dioxide was passed over the surface of the reaction mixture for four hours at room temperature. Dilute sodium hydroxide was added to the reaction mixture, the resulting solution warmed, and the aqueous layer filtered. Acidification of the filtrate with hydrochloric acid gave a precipitate which, after standing overnight, was collected on a filter paper (0.25 gm., about 35% yield). The 2,5-di-*t*-butylbenzoic acid after repeated recrystallizations from ethanol–water melted at 128° (lit. (15), 128°). Anal. Neutralization equivalent found: 237. Calc. for 2,5-di-*t*-butylbenzoic acid: 234.

*The Synthesis of 2,4,6-Tri-*t*-butylbenzoic Acid*

2,4,6-Tri-*t*-butylbromobenzene (1.4 gm.), 12 ml. of 0.1 molar *n*-butyllithium solution, and 25 ml. of absolute ether were refluxed together for one hour. Hydrolysis of a small amount of the reaction mixture with 10% hydrochloric acid gave a white crystalline product, which did not depress the melting point of authentic 1,3,5-tri-*t*-butylbenzene.

Dry carbon dioxide was passed over the reaction mixture for three hours. Sodium hydroxide (10%) was then added, the resulting solution warmed, filtered, and the filtrate acidified with hydrochloric acid. The mixture was allowed to stand overnight, then filtered (0.5 gm., 40% yield). The 2,4,6-tri-*t*-butylbenzoic acid, which crystallized from petroleum ether in thick white needles, melted at 297°. In a subsequent preparation a 60% yield was obtained. Anal. Found: C, 78.83, 78.75; H, 10.40, 10.53; N.E., 296, 292. Calc. for tributylbenzoic acid: C, 78.57; H, 10.41; N.E., 290.

2,4,6-Tri-*t*-butylbenzoic acid (0.1 gm.) was dissolved in 2.5 ml. of fuming sulphuric acid and after several minutes this solution was added slowly to 25 ml. of absolute methanol. Most of the methanol was removed under reduced pressure, 6 ml. of water added, and the remaining methanol removed, leaving a white precipitate. Water (100 ml.) was added to the residue and the solid methyl ester of 2,4,6-tri-*t*-butylbenzoic acid was isolated by filtration, washed with water, dried, and recrystallized from ethanol, m.p. 96–98° (yield 0.08 gm., about 80%).

When 0.01 gm. of the methyl ester of 2,4,6-tri-*t*-butylbenzoic acid was dissolved in fuming sulphuric acid and the resulting solution added to ice, the starting acid was regenerated.

*3,5-Di-*t*-butylbenzoic Acid*

A 500 ml. three-neck flask was fitted with a dropping funnel, stirrer, and gas trap. Aluminum chloride (7.3 gm.) and 10 ml. of carbon disulphide were placed in the flask and cooled with ice-salt to -10° . A solution of 15.6 gm. of 1,3,5-tri-*t*-butylbenzene in 8.5 gm. of acetyl chloride was added with stirring over a 45 min. period. The reaction mixture was then allowed to warm to room temperature and after two hours it was decomposed by adding it to water. The organic layer was separated and the solvent removed by evaporation, leaving a semisolid reaction product. This was cooled to -10° and filtered immediately. The white solid (0.4 gm.) thus isolated after recrystallization from ethanol melted at 69-72°. A mixed melting point with authentic 1,3,5-tri-*t*-butylbenzene showed this to be the starting material.

The filtrate from the filtration of the reaction product was a brown liquid, 3,5-di-*t*-butylacetophenone (wt. 4.2 gm.). The 2,4-dinitrophenylhydrazone of the ketone was prepared and after recrystallization from ethanol the derivative melted at 212-214°.

One gram of 3,5-di-*t*-butylacetophenone was dissolved in 20 ml. of dioxane, 10 ml. of 10% sodium hydroxide added, then iodine-potassium iodide solution until the dark color of iodine remained for over five minutes at 60° . The dark color was removed by the addition of a little 10% sodium hydroxide, water was then added until no more cloudiness appeared, and after 15 min. the solution was filtered and the filtrate acidified. The precipitate, which formed in the filtrate on standing overnight, was isolated by filtration. After two recrystallizations from ethanol-water the 3,5-di-*t*-butylbenzoic acid melted at 173-174°. Carpenter and Easter (6) report 169.5-170.5° as the melting point of their 3,5-di-*t*-butylbenzoic acid prepared by the oxidation of 3,5-di-*t*-butyltoluene. Anal. Found: N.E., 234. Calc. for dibutylbenzoic acid: N.E., 234.

Measurement of the Ionization Constants

The ionization constants (Table I) were measured by the method of Hammond and Hogle (9) in 50 volume % methanol-water solution at 21° using a Beckman pH meter with calomel and glass electrodes, standardized against buffer solutions of pH 4 and 10. About 0.01 meq. of the acid was dissolved in 10 ml. of 50% methanol and titrated with 0.0095 *N* methanolic NaOH. In the case of 2,4,6-tri-*t*-butylbenzoic acid, a saturated solution of the acid in 50% methanol was used.

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HEAT OF HYDROLYSIS OF URANIUM (IV) IN PERCHLORIC ACID SOLUTIONS¹

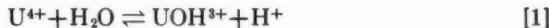
BY R. H. BETTS

ABSTRACT

The heat of hydrolysis of uranium (IV) in perchloric acid solution has been measured by a spectrophotometric technique. A value of 10.7 ± 1 kcal. per mole was obtained, in good agreement with a previous value determined by a calorimetric method. The entropy of association of uranium (IV) with hydroxyl ion is +52 e.u.

INTRODUCTION

In a kinetic study of the oxidation of uranium (IV) by iron (III) (1), a value was required for the heat of hydrolysis of uranium (IV). This quantity, ΔH , is related to the temperature variation of the hydrolysis constant K for reaction [1] according to $d(\ln K)/dT = \Delta H/RT^2$.



The hydrolysis constant K is defined by:

$$(UOH^{3+})(H^+)/[U^{4+}] = K, \quad [2]$$

where the brackets indicate concentrations in gram-ions per liter.

A value of 11 kcal./mole has been reported for ΔH (2). This result is based on the difference between the measured heats of solution of solid uranium tetrachloride in 0.5 M perchloric acid and in water. The accuracy of the value obtained by this method depends on the assumptions that:

- (i) UOH^{3+} is the only species of uranium (IV) in very dilute acid solutions,
- (ii) U^{4+} is the only uranium species in 0.5 M perchloric acid solution, and
- (iii) chloride ion does not form complex ions with uranium (IV).

However, Kraus and Nelson (3) have shown in a careful study of equilibrium [1] at 25°C. that none of these assumptions is strictly correct. Further, the precision of the value of 11 kcal./mole depends on a single measurement of the heat evolved when uranium tetrachloride is dissolved in water (2).

In the present work, the value of ΔH has been calculated more directly from measurement of the hydrolysis constant K as a function of temperature. The method used depends on measurement of the changes in optical density of partially hydrolyzed uranium (IV) solutions with temperature, and is based on the technique described in Reference (3). The principle of the method may be summarized.

The optical density D for a 1-cm. thickness of solution containing U^{4+} and UOH^{3+} as the only light-absorbing species is

$$D = (U^{4+})E_4 + (UOH^{3+})E_3, \quad [3]$$

where E_3 and E_4 are the extinction coefficients of UOH^{3+} and U^{4+} , respectively.

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for the wave length used. If the total concentration of uranium (IV) is *a* molar, then the hydrolysis constant *K* is given by:

$$K = (H^+)(E_4 - E_{obs}) / (E_{obs} - E_3), \quad [4]$$

where E_{obs} = observed extinction coefficient
 $= D/a$.

It follows from equation [4] that if E_4 and E_3 are known, measurements of E_{obs} and (H^+) permit the calculation of *K*. Kraus and Nelson (3) have shown that their data at 648 m μ (the wave length at the maximum of a characteristic U⁴⁺ absorption peak) are best described by $E_4 = 60.0$ and $E_3 = 6.1$, independent of ionic strength.

The principal assumption made in the application of this method to the present work is that the activity coefficient terms, which are implicit in the definition of the hydrolysis constant by equation [2], are unaffected by changes in temperature between 15.2°C. and 24.7°C. The assumption, although not strictly correct, is frequently made in other studies of similar equilibria (see, for example, Reference (4)). A second assumption is that the extinction coefficients E_3 and E_4 are temperature-independent. Further discussion bearing on this latter assumption is given below.

EXPERIMENTAL

Solutions of U^{IV} of the desired concentration and acidity were prepared by dilution of weighed portions of a stock solution 0.0787 M in U^{IV}, 1.010 M in perchloric acid. Other details of the preparation and analysis of the solutions are given elsewhere (1).

Two series of experiments have been made. (i) The first set were carried out with 2.44 M perchloric acid. At this concentration of acid, the hydrolysis of U⁴⁺ is very largely suppressed ($K \sim 0.01$ at 25°C. (3)). Such measurements served therefore to fix the value of E_4 , the extinction coefficient of U⁴⁺. (ii) The second set of experiments, made with 0.104 M perchloric acid, provided the values of E_{obs} required for the calculation of *K* as a function of temperature.

The optical measurements were made with a Beckman DU spectrophotometer. The instrument was adapted to permit control of the temperature of solutions in the cell compartment to $\pm 0.05^\circ\text{C}$. in the temperature range used here. The optical density at 648 m μ was read vs. a blank cell containing either 0.10 M or 2.44 M perchloric acid. The two 1-cm. cells used were matched to $\pm 0.1\%$ transmission at this wave length.

The optical density for solutions 2.44 M in perchloric acid showed no tendency to drift with time. However a slight decrease with time was noted for the solutions 0.104 M in perchloric acid, presumably as a result of slow air oxidation of U^{IV} which is known to occur more readily in solutions of low acidity. For these samples, the readings of optical density vs. time were extrapolated back to the time of preparation of the samples. These extrapolated values never differed by more than 0.5% from the optical density first recorded.

RESULTS AND DISCUSSION

Tables I and II give the relevant data for solutions 2.44 M and 0.104 M in

perchloric acid. The excellent agreement of our value of 59.9 ± 0.05 for E_4 at 25°C . with the value of 60.0 (3) is to be noted (Table I). However, the apparent dependence of E_4 on temperature (-0.2% per degree) shown in Table I is unexpected. To account for this relatively large change in the optical density on the basis of hydrolysis alone, it would be necessary to assume that the true value of E_4 is 63 or 64, and that $K = 0.14$ at 25°C . Such a value of K is 10 to 15 times higher than one would expect from the careful work of Kraus and Nelson. A more reasonable explanation is that K is indeed of the order of 0.01 at 25°C ., and that the extinction coefficient of U^{4+} is temperature dependent. This uncertainty in interpretation fortunately does not appreciably alter the value of ΔH calculated from the experimental results. (See below.)

TABLE I
EXTINCTION COEFFICIENTS* OF URANIUM (IV)
IN 2.44 M PERCHLORIC ACID

Temp., °C.	<i>M</i> U ^{IV} ($\times 10^3$)	E_4	E_4 (average)
24.7	8.56	59.9	
24.7	8.57	60.0	59.9 ₁
20.4	8.47	60.4	
20.4	8.52	60.6	60.5
15.2	8.51	61.1 ₁	
15.2	8.49	61.3	61.2

Ionic strength = 2.53.

*For $\lambda = 648 \text{ m}\mu$.

†This sample was heated to 24.7°C ., and gave $E_4 = 59.9$. On cooling again to 15.2°C ., $E_4 = 61.3$, indicating a reversible change.

TABLE II
EXTINCTION COEFFICIENTS* OF URANIUM (IV)
IN 0.104 M PERCHLORIC ACID

Temp., °C.	<i>M</i> U ^{IV} ($\times 10^3$)	E_{obs}	E_{obs} (average)
24.7	8.47	38.6 ₁	
24.7	8.50	38.6 ₂	38.6 ₁
20.4	8.49	42.2 ₂	
20.4	8.52	42.5 ₂	42.3 ₂
15.2	8.50	46.5 ₂	
15.2	8.52	46.4 ₂	46.5 ₁

Ionic strength = 0.19 (including contribution from $\text{U}(\text{ClO}_4)_4$).

*For $\lambda = 648 \text{ m}\mu$.

Table III gives the values of the hydrolysis constants calculated from the experimental results by means of equation [4]. Since $E_{\text{obs}} \gg E_3$, an error of $\pm 20\%$ in E_3 has only a small effect on ΔH , and the Kraus and Nelson value of 6.1 (3) has therefore been accepted for this constant. Because of the uncertainty regarding possible variations of E_4 with temperature, K has been calculated using three sets of values for E_4 . The second and third columns of Table III give the values of K based on $E_4 = 64$ and 63 respectively. In the last column are shown values of K deduced on the basis that E_4 is temperature-dependent. In this case, the appropriate value of E_4 for each temperature is given in Table I. The values of ΔH listed in Table III were calculated from a plot of

TABLE III
VALUES FOR THE EQUILIBRIUM CONSTANT AND ΔH FOR
HYDROLYSIS OF URANIUM (IV)

Temp., °C.	K^*	K^\dagger	K^\ddagger
24.7	0.0810	0.0778	0.0680
20.4	0.0619	0.0591	0.0519
15.2	0.0450	0.0424	0.0378
ΔH , kcal./mole = 10.5		10.9	10.6

Ionic strength = 0.19.

*Assuming $E_4 = 64$.

†Assuming $E_4 = 63$.

‡Assuming E_4 is temperature-dependent.

$\log K$ vs. $1/T^\circ K$. (Fig. 1). The values of ΔH obtained from these three sets of values of K are identical within experimental error, i.e., 10.7 ± 1.0 kcal./mole.

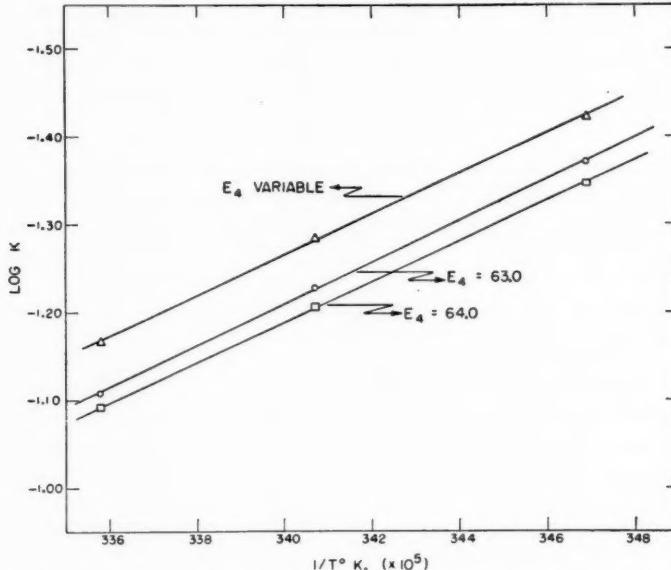


FIG. 1. Dependence of the hydrolysis constant on temperature (Table III).

The agreement of this result with that found earlier (2) is striking, in view of the completely different experimental methods employed; however the almost exact coincidence of the two values must be regarded as fortuitous.*

Table III shows that K is about 0.075 at $24.7^\circ C$., the exact value depending on the value of E_4 assumed. For comparison, the Kraus and Nelson result (3) is 0.05 at $25^\circ C$., for ionic strength 0.19. This agreement is as good as can be

*NOTE ADDED IN PROOF: In a paper published after completion of present manuscript, Kraus and Nelson (*J. Am. Chem. Soc.* 77:3721, 1955) report $\Delta H = 11.7$ kcal./mole for heat of hydrolysis of uranium (IV) in perchlorate media, in agreement with value obtained in present work.

expected, since in the present study, uranium (IV) perchlorate contributes almost 50% of the total ionic strength at $\mu = 0.19$, whereas the value of 0.05 applied to solutions in which sodium perchlorate and perchloric acid were the principal electrolytic components.

The entropy of association of U^{4+} with a hydroxyl ion can now be estimated. For this purpose the hydrolysis constant at zero ionic strength, K_a , must be used— 0.21 ± 0.02 at 25°C . (3). Using the relation $\Delta F^\circ = -RT \ln K_a$, and $\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$, ΔS° and ΔF° at 25°C . are found to be +33 e.u. and +0.92 kcal./mole, respectively. These values refer to reaction [1] above. This result may be combined with the dissociation equilibrium of water (4) to derive the thermodynamic constants for the association reaction proper:

	ΔF° , kcal.	ΔH° , kcal.	ΔS° , e.u.
$U_{\text{aq}}^{4+} + \text{H}_2\text{O} \rightarrow \text{UOH}_{\text{aq}}^{3+} + \text{H}_{\text{aq}}^+$	+0.9	+11.0	+33
$\text{H}_{\text{aq}}^+ + \text{OH}_{\text{aq}}^- \rightarrow \text{H}_2\text{O}$	-19.1	-13.5	+19
$U_{\text{aq}}^{4+} + \text{OH}_{\text{aq}}^- \rightarrow \text{UOH}_{\text{aq}}^{3+}$	-18.2	-2.5	+52

The large positive value of ΔS° for the association reaction is in qualitative agreement with the suggestion of Rabinowitch and Stockmayer (4), viz., the partial neutralization of charge which occurs releases water molecules from the hydration shells around the separated ions, and thereby increases the disorder (and hence the entropy) of the system as a whole.

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KINETICS OF THE OXIDATION OF URANIUM (IV) BY IRON (III) IN AQUEOUS SOLUTIONS OF PERCHLORIC ACID¹

By R. H. BETTS

ABSTRACT

The kinetics of oxidation of uranium (IV) by iron (III) in aqueous solutions of perchloric acid have been investigated at four temperatures between 3.1°C. and 24.8°C. The reaction was followed by measurement of the amount of ferrous ion formed. For the conditions $(H^+) = 0.1\text{--}1.0 M$, ionic strength = 1.02, $(Fe^{III}) = 10^{-4}\text{--}10^{-5} M$, and $(U^{IV}) = 10^{-4}\text{--}10^{-5} M$, the observed rate law is

$$d(Fe^{II})/dt = -2d(U^{IV})/dt = 2(U^{IV})(Fe^{III}) \left[\frac{K'(H^+) + K''}{(H^+)^2 + (K_1 + K_2)(H^+) + K_1 K_2} \right] \text{mole/liter/sec.}$$

K_1 and K_2 are the first hydrolysis constants for Fe^{3+} and U^{4+} , respectively, and K' and K'' are pseudo rate constants. At 24.8°C., $K' = 2.98 \text{ sec.}^{-1}$, and $K'' = 10.6 \text{ mole liter}^{-1} \text{ sec.}^{-1}$. The corresponding temperature coefficients are $\Delta H' = 22.5 \text{ kcal./mole}$ and $\Delta H'' = 24.2 \text{ kcal./mole}$. The kinetics of the process are consistent with a mechanism which involves, as a rate-controlling step, electron transfer between hydrolyzed ions.

INTRODUCTION

Oxidation-reduction reactions between cations in aqueous solution have been thought until recently to proceed very rapidly, and the term "instantaneous" has frequently been used to characterize their rates. However recent studies with radioactive tracers have shown that even such elementary reactions as electron transfer between iron (II) and iron (III), or between Ce (III) and Ce (IV), do not proceed instantaneously (18, 8). Such results have reawakened interest in the whole subject of both isotopic and nonisotopic electron transfer reactions between cations in solution. Some kinetic information is now available relating to the reactions between the nonisotopic pairs Sn (II) - Fe (III) (5), Tl (III) - Fe (II) (2), and Np (IV) - Fe (III) (10). Several review articles have recently appeared in which the current status of theory and experiment have been summarized for both isotopic and nonisotopic electron transfer reactions (1, 14, 19). The proceedings of a symposium held in 1954 on this subject have also been published (12).

As a further example of this type of reaction, the present paper describes experiments relating to the kinetics of the oxidation of uranium (IV) by iron (III) in aqueous acidic media. Perchloric acid and sodium perchlorate were chosen as the principal electrolytes, since amongst the common inorganic anions, perchlorate has the least tendency to form ion-pairs with cations. To bring the rate of reaction into a range suitable for study, it has been necessary to work with solutions 10^{-4} to $10^{-5} M$ in uranium (IV) and iron (III).

The course of the reaction has been followed by measurement of the rate of formation of iron (II). Such measurements, in conjunction with a knowledge of the stoichiometry of the reaction, were sufficient to enable a kinetic analysis of the results to be made. It would have been useful, as confirmatory evidence,

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to measure also the rate of disappearance of uranium (IV). However no method could be devised which was specific for uranium (IV) at the low concentrations involved.

EXPERIMENTAL

A. Reagents

Doubly distilled water was used in the preparation of all reagents and in all experiments in the present investigation.

Uranyl perchlorate was prepared by dissolving reagent grade uranium trioxide in an excess of standard perchloric acid. An aqueous solution of uranium (IV) perchlorate was prepared from this solution by electrolytic reduction of the uranium at a mercury cathode in a two compartment cell. The uranium (IV) content was determined by titration with standard potassium permanganate.

Sodium perchlorate, which was used to adjust the ionic strength of solutions as required, was prepared from reagent grade stock by two recrystallizations from water.

A stock solution of iron (III) perchlorate was prepared by methods described previously (4). Solutions of iron (II) perchlorate, which were required for standardization of the analytical procedures used in the kinetic experiments, were made by dissolving iron (II) ammonium sulphate in 1.0 M perchloric acid, and were standardized against potassium permanganate.

All other chemicals used were reagent grade, and were not further purified.

B. Procedure

Unless indicated otherwise, all experiments were made with solutions of ionic strength 1.02.

The kinetic experiments were carried out in glass-stoppered flasks which were suspended in a water bath at the desired temperature. All of the reagents except uranium (IV) were added to the flask, after which the required amount of this reactant was added carefully by micropipette. The reaction was started by inverting the flask, and mixing thoroughly the added uranium (IV) with the rest of the solution.

The course of the reaction was followed by measurement of the amount of iron (II) formed as a function of time. For this purpose, 4 to 5 ml. samples were withdrawn at measured times, and run rapidly into a mixture which stopped the reaction, and which also served as a means for analysis of ferrous ion formed (see below). Generally eight samples were taken during each experiment, together with two more when the reaction had gone to completion. The purpose of the last two samples was to give an independent measure of the initial concentration of either uranium (IV) or iron (III), depending on which of these two was in excess initially. In most of the experiments, iron (III) was in large excess over uranium (IV), and hence the final measurement of ferrous ion formed was used as a measure of the initial concentration of uranium (IV) ion. Confirmatory evidence regarding the validity of this procedure is given later.

The quenching mixture referred to above consisted of 5 ml. of an aqueous

solution of *o*-phenanthroline; it contained also an equimolar mixture of ammonium fluoride and ammonium acetate in sufficient quantity to raise the pH of the final reaction mixture to 4.0. At this pH, *o*-phenanthroline reacts immediately with ferrous ion to form the highly colored complex $\text{Fe}(\text{o-phen})_3^{++}$. The concentration of this complex was determined by measurement of the optical density at 511 m μ of portions of the quenched mixture with a Beckman DU spectrophotometer. The exact dilution of the reacting mixture by the quenching solution was calculated from the weight of the latter before and after addition of the sample for analysis.

The analytical scheme was calibrated by addition of known amounts of iron (II) perchlorate to solutions similar to those used in the kinetic studies. A small blank was observed which depended on the total amount of iron (III) present. This was taken into account as required. The presence of either uranium (IV) or uranium (VI) had no measurable effect on the analysis. Separate experiments showed that the quenching agent did not induce the oxidation of uranium (IV) by iron (III); it was also shown that ferrous ion has no tendency to form in quenched solutions containing both uranium (IV) and iron (III).

The detailed mechanism of the quenching action of this mixture is not completely understood. However, the omission of ammonium fluoride from the mixture completely destroys the quenching action; it is probable therefore that the reaction is stopped by fluoride ion complexing of the reactants at pH 4.0.

C. Experimental Results

(i) Stoichiometry of the Reaction

Table I presents the data for seven experiments relating to the stoichiometry of the reaction. The initial concentrations of reactants in each experiment were calculated from the amounts of standardized stock solutions used. In column four is given the final concentrations of iron (II) found when the reaction had gone to completion. Each value in this column is based on at least two con-

TABLE I
STOICHIOMETRY OF THE REACTION

Run No.	$(\text{U}^{\text{IV}})_0, M \times 10^6$	$(\text{Fe}^{\text{III}})_0, M \times 10^6$	$\text{Fe}^{2+}, M \times 10^6$	
			Found	Calc.
1	3.75	52.4	7.30	7.50
3	3.72	21.1	7.26	7.44
4	3.63	10.60	7.04	7.26
5	9.10	10.65	10.57	10.65
6	9.10	5.41	5.41	5.41
7	18.20	2.26	2.27	2.26
8	36.20	1.21	1.22	1.21

cordant analyses which were made on samples taken several hours apart. Values of iron (II) concentrations given in column five are those calculated according to



The slight differences between the corresponding values in columns four and

five of Table I are not greater than the combined probable errors involved; it is concluded therefore that Equation [1] represents the stoichiometry of the reaction.

(ii) *Kinetic Order of the Reaction*

Experiments which were made to deduce the kinetic order of the reaction are summarized in Table II. These experiments were carried out at a perchloric acid concentration of 1.021 M, at 24.8°C. The second order rate constant k_0 shown in the last column of Table II is defined by Equation [2]:

$$\frac{+d(\text{Fe}^{II})}{dt} = \frac{-d(\text{Fe}^{III})}{dt} = \frac{-2d(\text{U}^{IV})}{dt} = 2k_0 (\text{U}^{IV})(\text{Fe}^{III}). \quad [2]$$

The constant k_0 was calculated from the results in the following way. If $(\text{U}^{IV})_0$ and $(\text{Fe}^{III})_0$ represent the total concentrations of these species at time zero,

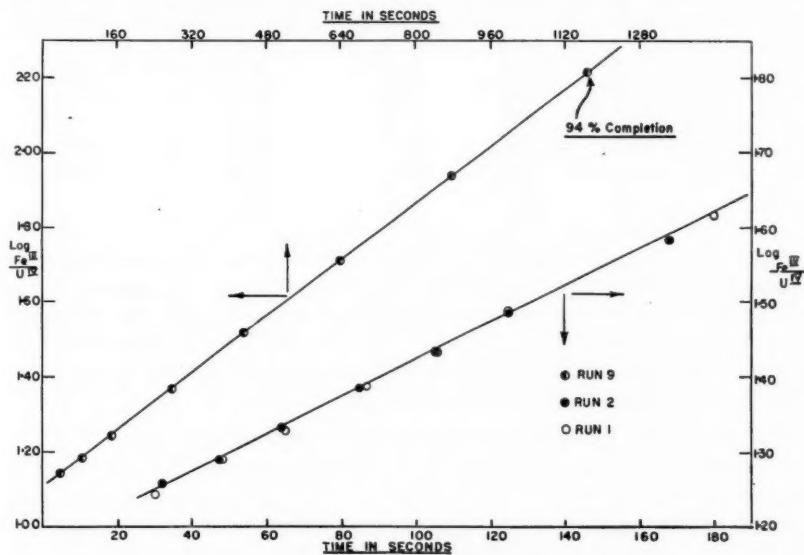


FIG. 1. Plot illustrating second order behavior of the reaction.

and if $(\text{Fe}^{II})_t$ is the concentration of iron (II) measured at time t , then the corresponding concentrations of reactants are given by:

$$(\text{U}^{IV}) = (\text{U}^{IV})_0 - 0.5(\text{Fe}^{II})_t, \quad [3]$$

$$(\text{Fe}^{III}) = (\text{Fe}^{III})_0 - (\text{Fe}^{II})_t. \quad [4]$$

Substitution of Equations [3] and [4] into [2] and integration in terms of (Fe^{II}) leads to

$$k_0 t = \frac{2.303}{(\text{Fe}^{III})_0 - 2(\text{U}^{IV})_0} \log \frac{(\text{Fe}^{III})_0}{(\text{U}^{IV})_0} + B, \quad [5]$$

where B is an integration constant related to the (arbitrary) initial concen-

trations of uranium (IV) and iron (III). Equation [5] implies that a plot of $\log (\text{Fe}^{\text{III}})/(\text{U}^{\text{IV}})$ vs. t should give a straight line if the reaction is of first order in both iron (III) and uranium (IV). Fig. 1 shows such plots for the data of Runs 1, 2, and 9 of Table II. In these cases, and for all experiments in this study, such plots gave good straight lines up to at least 80% completion of the reaction. Table II shows also that the value of k_0 deduced from the slope of these plots is unaffected by a 30-fold variation in $(\text{U}^{\text{IV}})_0$, and a 40-fold variation in $(\text{Fe}^{\text{III}})_0$. We conclude therefore that at constant hydrogen-ion concentration, the reaction is first order with respect to both uranium (IV) and iron (III).

TABLE II
VALUES OF SECOND ORDER RATE CONSTANT AT 24.8°C.
 $(\text{HClO}_4) = 1.021 M; \mu = 1.02$

Run No.	$(\text{Fe}^{\text{III}})_0, M \times 10^5$	$(\text{U}^{\text{IV}})_0, M \times 10^5$	$k_0, (\text{mole}^{-1} \text{liter}^1 \text{sec.}^{-1})$
1	52.4	3.75	12.9
2	52.4	3.72	12.9
3	21.1	3.72	12.7
4	10.6	3.63	12.2
5	10.6	9.10	11.9
6	5.41	9.10	10.8
7	2.26	18.2	11.5
8	1.21	36.2	13.2
9	21.1	1.69	12.4
10	21.1	3.13	12.6

Fig. 1 also gives some idea of the reproducibility of the kinetic experiments. Evidently the slope of the $\log (\text{Fe}^{\text{III}})/(\text{U}^{\text{IV}})$ vs. t plot can be reproduced to $\pm 2\%$. However the derived rate constant is not known with this precision, since it also depends on the difference $(\text{Fe}^{\text{III}})_0 - 2(\text{U}^{\text{IV}})_0$. Judging from the spread of results in Table II, an over-all uncertainty of $\pm 4\text{--}5\%$ is associated with the rate constants obtained in this work.

(iii) Dependence of the Rate on Hydrogen-ion Concentration

Table III summarizes the results for experiments at varying concentrations of hydrogen ion, for each of four temperatures. The ionic strength of each solution was maintained at 1.02 by addition of sodium perchlorate as required. For each run a good straight line was observed when $\log (\text{Fe}^{\text{III}})/(\text{U}^{\text{IV}})$ was plotted vs. t . From the slope of such plots, the corresponding second order rate constants shown in Table III were calculated.

TABLE III
VALUES OF SECOND ORDER RATE CONSTANT k_0 AS A FUNCTION OF
ACIDITY AND TEMPERATURE

Temp., °C.	HClO ₄ , M					
	1.021	0.821	0.6167	0.4125	0.2083	0.1045
24.8	12.3*	19.2	30.7	64.7	233	—
16.8	4.16	6.57	10.4	21.8	74	304
7.8	1.17	1.81	2.92	6.15	22.4	80
3.1	0.54	0.82	1.36	3.01	10.3	33.6

*Average of 10 values listed in Table II.
The units of k_0 are $\text{mole}^{-1} \text{liter}^1 \text{sec.}^{-1}$.

The apparent order of the reaction with respect to hydrogen ion at each temperature has been calculated from these results by using the following empirical rate expression:

$$\text{Rate} = 2k'[\text{H}^+]^n [\text{U}^{IV}][\text{Fe}^{III}]. \quad [6]$$

In Equation [6], $k'[\text{H}^+]^n$ is to be identified with k_0 for each experiment. The value of n can therefore be deduced from a plot of $\log k_0$ vs. $\log [\text{H}^+]$ for each temperature. These plots are shown in Fig. 2, from which it was found that n

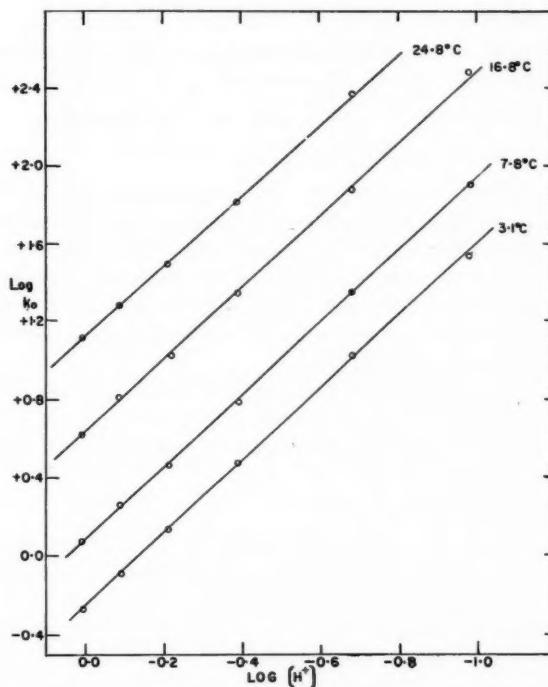


FIG. 2. Variation of the observed rate constant k_0 with temperature and acidity.

has a value of -1.81 ± 0.02 , independent of temperature. This result implies that the rate of oxidation of uranium (IV) by iron (III) is dependent on very nearly the inverse second power of the hydrogen-ion concentration.

(iv) Effect of Ionic Strength on the Reaction

A few experiments were made to determine the effect of an inert electrolyte (sodium perchlorate) on the rate of the reaction. The results of these experiments are summarized in Table IV. Evidently, the rate of the reaction increases slowly with ionic strength in the region $\mu = 0.4$ to $\mu = 1.02$.

TABLE IV

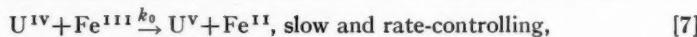
EFFECT OF IONIC STRENGTH ON RATE OF REACTION AT 5°C.
 $\text{HClO}_4 = 0.413 M$; $(\text{Fe}^{III})_0 = 2.11 \times 10^{-4} M$; $(\text{U}^{IV})_0 = 2.3 \times 10^{-5} M$

NaClO_4 M	μ	k_0 (mole $^{-1}$ liter $^{+1}$ sec. $^{-1}$)
0.0	0.414	3.57
0.195	0.609	3.96
0.405	0.819	4.06
0.609	1.023	4.35

DISCUSSION

Stoichiometry and Kinetic Order of the Reaction

The kinetic order of the reaction at constant acidity and the stoichiometry of the process are most simply accounted for by the following scheme:



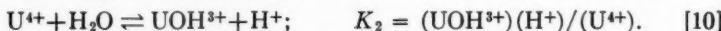
U^V represents an undetermined form of pentavalent uranium (11). These equations have not been balanced with respect to hydrogen ion, nor are the ionic configurations of the reactants specified. These aspects are discussed further below. Assuming that $d(\text{U}^V)/dt = 0$, this scheme leads directly to the observed rate expression (Equation [2] above). The factor 2 in Equation [2] arises from the fact that for every $\text{Fe}(\text{II})$ formed in Reaction [7], a second $\text{Fe}(\text{II})$ is formed by Reaction [8].*

The absence of terms like $(\text{U}^{IV})^2$ or $(\text{Fe}^{III})^2$ in the empirical rate expression rules out any significant contribution from dimeric ions, e.g., $(\text{FeOHFe})^{+5}$; this ion is known to be present at very low concentration in aqueous solutions of ferric salts (9, 15).

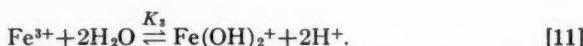
Effect of Hydrogen-ion Concentration

The appearance of the nonintegral order $[\text{H}^+]^{-1.81}$ in the rate expression suggests that at least two paths involving hydrolyzed ions contribute to the slow stage of the reaction. The slight departure of this exponent from -2.00 points to the principal path as one involving two hydroxyl groups, with some minor participation from reactions involving only one hydroxyl group.

The principal hydrolyzed species present in solution are FeOH^{2+} and UOH^{3+} (15, 17, 13), which exist in equilibrium with the parent fully hydrated ions according to:

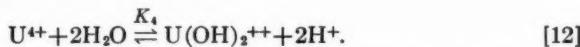


The doubly hydrolyzed ion $\text{Fe}(\text{OH})_2^+$ is also present at very low concentration (8, 9, 16, 17):

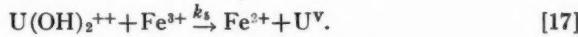
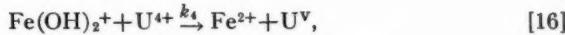
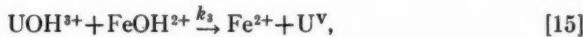
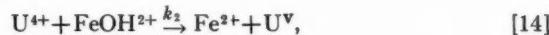


*A rapid disappearance of U^V by disproportionation according to: $2\text{U}^V \rightarrow \text{U}^{VI} + \text{U}^{IV}$ would also satisfy the observed stoichiometry and kinetic order. This reaction is known to be rapid in solutions of high acidity (11). However the low concentration of U^V makes it unlikely that this mechanism would compete favorably with Reaction [8] above.

Although there is no quantitative information available, it is reasonable to assume, by analogy with the chemistry of iron (III), that the ion $\text{U}(\text{OH})_2^{++}$ also is present at very low concentration:



The rate-controlling step (Equation [7] above) may therefore consist of the following competitive reactions:



Reactions [13] and [14] involve one hydroxyl group and are of course kinetically indistinguishable. The remaining reactions, which involve two hydroxyl groups, are also kinetically equivalent. These two groups of processes are referred to below as the 1-OH and the 2-OH processes, respectively.*

The following rate expression is derived on the basis of these postulated reactions:

$$\frac{d(\text{Fe}^{2+})}{dt} = 2 (\text{U}^{IV})(\text{Fe}^{III}) \frac{K'(\text{H}^+) + K''}{(\text{H}^+)^2 + (K_1 + K_2)(\text{H}^+) + K_1 K_2}. \quad [18]$$

Equation [18] is based on the assumption that the concentrations of the species $\text{U}(\text{OH})_2^{++}$ and $\text{Fe}(\text{OH})_2^{+}$ are negligible in comparison to the total concentration of uranium (IV) and iron (III). In this equation:

$$K' = k_1 K_2 + k_2 K_1, \quad [19]$$

$$K'' = k_3 K_1 K_2 + k_4 K_3 + k_5 K_4. \quad [20]$$

Equation [18] describes the variation of the observed rate constant k_0 with acidity (Table III) provided:

$$k_0 = \frac{K'(\text{H}^+) + K''}{(\text{H}^+)^2 + (K_1 + K_2)(\text{H}^+) + K_1 K_2}. \quad [21]$$

If the denominator on the right-hand side of Equation [21] is represented by D , then

$$k_0 D = K'[\text{H}^+] + K''. \quad [22]$$

The left-hand side of Equation [22] can be calculated from the results in Table III together with a knowledge of the hydrolysis constants K_1 and K_2 . The appropriate values of K_1 and K_2 for each temperature were calculated from

*In reactions [13] to [17] the products have been written as Fe^{2+} and UV ; if, as is probable, uranium (V) exists in solution as UO_2^{3+} , one or more rapid hydrolyses may take place following electron transfer between the reactant ions indicated in the L.H.S. of these equations. It is not possible to specify the exact sequence of these hydrolytic reactions, nor for the present purpose, is it necessary.

data in the literature (17, 15, 3, 6, 13), and are given in Table V. A test of Equation [22] can therefore be made, since a plot of $k_0 D$ vs. $[H^+]$ should give a straight line, with a finite intercept. Fig. 3 shows the data from the present

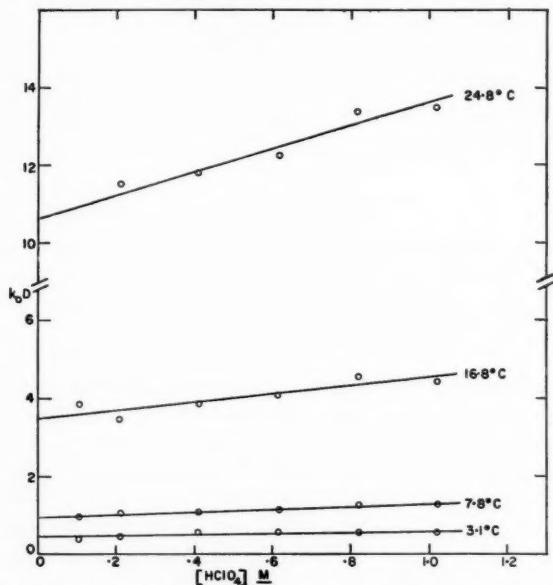


FIG. 3. Application of Equation [22] to the experimental results.

work treated in this manner. Within experimental error, Equation [22] describes the results at each temperature, and lends support to the suggestion that a duality of mechanism is involved in the rate-controlling step of the process.

TABLE V
VALUES OF THE HYDROLYSIS CONSTANTS K_1 AND K_2

Temp., °C.	K_1 , mole liter ⁻¹ ($\times 10^3$)	K_2 , mole liter ⁻¹ ($\times 10^3$)
3.1	0.311	6.8
7.8	0.452	9.4
16.8	0.85	17.0
24.8	1.59	27.8
25.0	1.61*	28.2†

*Value at 25.0°C. from Ref. (15), for $\mu = 1.02$.

†Value at 25.0°C. from Ref. (13), for $\mu = 1.02$.

Values at other temperatures calculated from

$$\Delta H_1 = 12.3 \text{ kcal./mole} \quad (17)$$

$$\text{and } \Delta H_2 = 10.6 \text{ kcal./mole} \quad (5)$$

according to $d \ln K/dt = \Delta H/RT^2$.

K_1 and K_2 are defined by Equations [9] and [10] in the text.

Values of the constants K' and K'' at each temperature can be obtained from the slopes and intercepts, respectively, of the lines in Fig. 3. These values

are given in Table VI. The variation of these pseudo rate constants with temperature is shown in Fig. 4, in which are plotted $\log K'$ or $\log K''$ vs. $1/T^\circ\text{K}$.

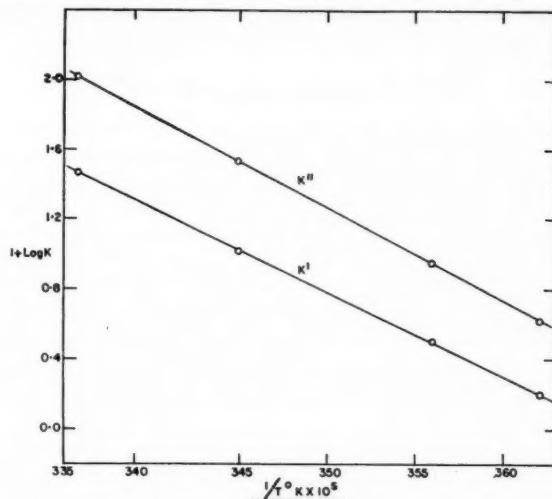


FIG. 4. Variation of the pseudo rate constants K' and K'' with temperature.

From the slopes of these lines, values of the corresponding temperature coefficients $\Delta H'$ and $\Delta H''$ were found to be 22.5 and 24.5 kcal./mole, respectively. These ΔH terms may be thought of as the apparent energies of activation for the 1-OH and 2-OH processes.

TABLE VI
VALUES OF THE PSEUDO RATE CONSTANTS K' AND K''

Temp., $^\circ\text{C}.$	K' (sec. $^{-1}$)	K'' (mole liter $^{-1}$ sec. $^{-1}$)
3.1	0.158	0.420
7.8	0.320	0.936
16.8	1.05	3.48
24.8	2.98	10.6

K' and K'' are defined by Equations [19] and [20] in the text.

The relative contributions of the 1-OH and 2-OH processes can be assessed from the values of K' and K'' . For example, at $24.8^\circ\text{C}.$, in 1.021 M perchloric acid, the mechanisms involving two hydroxyl groups make up 78% of the total reaction.

The positive identification of the constants K' and K'' with the rate constants for the individual processes shown in Equations [13] to [17] cannot of course be made with any certainty. This is evident from Equations [19] and [20] which define K' and K'' . However, two points emerge from a more detailed examination of the results.

(i) A possible assumption would be that since $\text{Fe}(\text{OH})_2^+$ and $\text{U}(\text{OH})_2^{++}$ are present in very low concentration, they contribute nothing to the reaction, i.e., k_4 and $k_5 = 0$. The apparent energy of activation $\Delta H''$ for the 2-OH process would then be:

$$\Delta H'' = 24.2 \text{ kcal.} = E_3 + \Delta H_1 + \Delta H_2, \quad [23]$$

where ΔH_1 = heat of hydrolysis of iron (III),

ΔH_2 = heat of hydrolysis of uranium (IV),

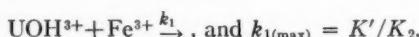
and E_3 = true energy of activation for the electron transfer reaction between UO^{3+} and FeO^{2+} (Reaction [15] above).

Since $\Delta H_1 = +12.3$ kcal./mole (17) and $\Delta H_2 = +10.6$ kcal./mole (3, 6), then E_3 could not be more than 1 or 2 kcal./mole. This is an extraordinarily low value for the activation energy of an electron transfer reaction between cations in solution (19). It is suggested therefore that the main contribution to the 2-OH process is *not* that indicated by Reaction [15], and that Reactions [16] and [17], involving $\text{Fe}(\text{OH})_2^+$ and $\text{U}(\text{OH})_2^{++}$, are the principal contributors to the 2-OH process.

This admittedly qualitative method of distinguishing between kinetically equivalent paths cannot be extended to the other 2-OH processes, since we have insufficient knowledge of the thermodynamics of formation of either $\text{U}(\text{OH})_2^{++}$ or $\text{Fe}(\text{OH})_2^+$.

(ii) We finally consider the relation between K' and the individual rate constants k_1 and k_2 for the 1-OH processes. The *maximum* values of these rate constants can be calculated from the experimental results in the following way:

(a) If $k_2 = 0$, the whole of the 1-OH contribution is carried by Reaction [13]:



(b) Similarly, if $k_1 = 0$, then $k_{2(\max)} = K'/K_1$.

Table VII gives the maximum values for k_1 and k_2 derived in this way, together with the corresponding energy and entropy of activation terms (E_{act} and ΔS^\ddagger , respectively). The E_{act} terms in Table VII were calculated from the value of $\Delta H'$ and either ΔH_1 or ΔH_2 , in a manner similar to that shown in Equation [23]. Values of ΔS^\ddagger were calculated from the data in columns two and three of Table VII by reaction rate theory (7).

TABLE VII
MAXIMUM VALUES OF RATE CONSTANTS k_1 AND k_2 AT 25°C.

Condition assumed	Rate constant, mole ⁻¹ liter ⁻¹ sec. ⁻¹	E_{act} , kcal./mole	ΔS^\ddagger , e.u./mole
$k_2 = 0$ $k_1 = K'/K_2$	107	11.9	-11.2
$k_1 = 0$ $k_2 = K'/K_1$	1860	10.2	-11.3

Perhaps the most significant feature of the results in Table VII is that E_{act} for either process is ~ 10 to 12 kcal./mole. Most of the simple cationic electron transfer reactions which have been examined in any detail yield values between 8 and 11 kcal./mole for this factor (19).

CONCLUSION

The principal conclusion of the present work is that the rate of reaction between iron (III) and uranium (IV) is controlled by the concentration of hydrolyzed forms of the reactants. Two independent paths appear to be present, the predominant one involving two hydroxyl groups. The experimental evidence suggests, but does not prove, that the reactions $\text{Fe}(\text{OH})_2^+ + \text{U}^{4+} \rightarrow$ and $\text{Fe}^{3+} + \text{U}(\text{OH})_2^{2+} \rightarrow$ predominate over the kinetically equivalent 2-OH path involving FeOH^{2+} and UOH^{3+} . The energy of activation for the 1-OH path is in qualitative agreement with other data for similar systems, and in this respect the result is unexceptionable.

The marked reactivity of hydrolyzed species in this system has also been observed in the other studies already cited. For example, the oxidation of neptunium (IV) by iron (III) requires the participation by three hydroxyl groups (10). Also, the conclusions we have reached regarding the presence of two concurrent paths for reaction find a counterpart in several other systems. Thus, the isotopic electron transfer reaction between iron (II) and iron (III) proceeds in perchlorate media via the pairs $\text{Fe}^{2+}-\text{Fe}^{3+}$ and $\text{Fe}^{2+}-\text{FeOH}^{2+}$; the rate constant for the reaction involving FeOH^{2+} is about 1000-fold greater than that for the reaction between the fully hydrated ions (18).

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THE VIBRATIONAL SPECTRA OF $\text{CH}_2=\text{CHCl}$ AND $\text{CH}_2=\text{CDCl}$ ¹

By J. C. EVANS² AND H. J. BERNSTEIN

ABSTRACT

The infrared and Raman spectra of $\text{CH}_2=\text{CDCl}$ and the Raman spectrum of $\text{CH}_2=\text{CHCl}$ have been obtained and depolarization ratios of the Raman bands have been measured. The spectra of the two molecules have been correlated.

While the vibrational assignment of vinyl chloride has been satisfactorily made with the aid of the observed envelopes of the infrared absorption bands (8), the vibrational spectrum of $\text{CH}_2=\text{CDCl}$ has not previously been examined. Since a sample of the latter compound was available in this laboratory, its vibrational spectrum was examined and correlated with that of vinyl chloride. Furthermore, since previous Raman studies (6) did not include depolarization measurements, the Raman spectrum of vinyl chloride was obtained and depolarization ratios measured.

EXPERIMENTAL

Samples of both compounds were provided by Mr. J. Francis and Dr. L. C. Leitch. A commercial sample (Matheson Co.) of vinyl chloride was distilled. The preparation of the deuterium substituted compound will be described (3). This sample contained a small amount of vinyl chloride which was detected spectroscopically.

The spectra were obtained with a Perkin-Elmer Model 112 double pass infrared spectrometer and a White, grating Raman spectrometer with photoelectric recording (9), using 4358 Hg as exciting line. The infrared spectrum of $\text{CH}_2=\text{CDCl}$ in the vapor phase was measured using LiF, CaF₂, NaCl, and CsBr optics and the Raman spectra of both compounds in the liquid phase were obtained at $-100^\circ\text{C.} \pm 5^\circ\text{C}$. A low temperature cell, in which the sample tube was cooled by a controlled stream of air passed through liquid nitrogen, was used. The cooled central part of the cell was surrounded by an evacuated jacket which in turn was surrounded by an outer jacket containing saturated aqueous sodium nitrite solution. The filter and the low temperature inhibited polymerization of the samples. Depolarization measurements were made by wrapping polaroid film around the entire cell, first with its axis parallel to the length of the sample tube and then at right angles (2). The observed ratios were corrected for convergence (7).

The Raman and infrared data for the two molecules are collected in Tables I and II. The Raman spectra are reproduced in Fig. 1, and Fig. 2 illustrates the infrared spectrum of $\text{CH}_2=\text{CDCl}$.

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TABLE I
RAMAN SPECTRUM OF $\text{CH}_2=\text{CHCl}$ (LIQUID)

Assignment	Approximate description	cm.^{-1}	$\rho_{\text{corr.}}$
$2\nu_4 (A')$		3203	0.33
ν_1	$\nu_{\text{as}} (\text{CH}_2); a'$	3112	0.75
ν_2	$\nu (\text{CH}); a'$	3079	0.46
ν_3	$\nu_s (\text{CH}_2); a'$	3027	0.25
$\nu_5 + \nu_6 + \nu_9 = 3033 (A')$		3014 sh.	0.22
$\nu_4 + \nu_5 = 2966 (A')$		2950	0.2
$\nu_{11} + \nu_{12} = 1523 (A')$	$\nu (\text{C}=\text{C}); a'$	1603	0.39
ν_5	$\text{CH}_2 \text{ def.}; a'$	1515	?
ν_6	$\text{CH rock.}; a'$	1363	0.63
$2\nu_{12} = 1246 (A')$		1274	0.60
ν_7	~ 1242 $\text{CH}_2 \text{ rock.}; a'$	1026	~ 0.76
ν_{11}	Out-of-plane; a''	901	~ 0.85
ν_8	$\nu (\text{C}-\text{Cl}); a'$	706	0.42
ν_{13}	Torsion; a''	623	Dp
ν_9	$\delta (\text{C}=\text{C}-\text{Cl}); a'$	396	0.52
ν_{10} , at 942.5 cm.^{-1} in the infrared, was not observed.			

*Fermi resonance.

TABLE II
THE INFRARED AND RAMAN SPECTRA OF $\text{CH}_2=\text{CDCl}$

cm. ⁻¹	Type	Assignment	Raman spectrum (liquid phase)	
			cm. ⁻¹	Corrected depolarization ratio
3535	?	$3186 + 385 = 3571 (A')$		
3430	$\overline{}$	a'	3034 + 385 = 3419 (A')	
3410	$\overline{}$			
3175 sh.	?	$2 \times 1593 = 3186 (A')$	3168	0.24
3133	$\overline{}$	a'	3110	0.77
3111	$\overline{}$			
3080 sh.		ν_2 of $\text{CH}_2=\text{CHCl}$ impurity	3079	~ 0.55
3045	$\overline{}$	a'	3020	0.33
3024	$\overline{}$	$\nu_3: \nu_s (\text{CH}_2)$		
2980	?	$2308 + 714 = 3022 (A')$	2985	P
2464	$\overline{}$	a'		
2453	$\overline{}$	$1117 + 1358 = 2476 (A')$		
2445	$\overline{}$			
2319	$\overline{}$	a'		
2308	$\overline{}$	$\nu_2: \nu (\text{C}-\text{D})$	2300	0.47
2299	$\overline{}$			
2230	$\overline{}$	a'		
2220	$\overline{}$	$2 \times 1117 = 2234 (A')$		
2210	$\overline{}$			
1812	$\overline{}$	a'		
1798	$\overline{}$	$2 \times 900 = 1800 (A')$		
1791	$\overline{}$			
~ 1730	?	$1358 + 385 = 1743 (A')$ or $2 \times 866 = 1732 (A')$ $2 \times 803 = 1606 (A')$ or $\text{CH}_2=\text{CHCl}$ impurity	1603	~ 0.7

TABLE II (*Concluded*)

Infrared spectrum (vapor phase)			Raman spectrum (liquid phase)		
cm. ⁻¹	Type	Assignment	cm. ⁻¹	Corrected depolarization ratio	
1604			1586	0.32	*
1593	<i>a'</i>	$\nu_4: \nu (\text{C}=\text{C})$	1530	P	
1584		$861 + 697 = 1558 (A')$	1493	P	
1498	<i>a'</i>	$385 + 1117 = 1502 (A')$	1437	Dp?	
1487		$587 + 861 = 1448 (A'')$	1395	P	
1478		$2 \times 714 = 1428 (A')$	1349	0.50	*
1427 sh.					
1406					
1367					
1358	<i>a'</i>	$\nu_5: \text{CH}_2 \text{ def.}$	1349	0.50	*
1347					
1292	<i>a'</i>	$\text{CH}_2=\text{CHCl}$ impurity			
1270					
1192	<i>a'</i>	$2 \times 587 = 1174 (A')$			
1165					
1125	<i>a'</i>	$\nu_7: \text{CH}_2=\text{CD}$ rocking	1100	0.35	
1117					
1104	<i>a'</i>	$385 + 587 = 972 (A'')$			
950		$\text{CH}_2=\text{CHCl}$ impurity			
943	<i>a''</i>				
900		ν_{10} out-of-plane	905	~ 0.83	
	<i>a''</i>	$\nu_6: \text{CH}_2=\text{CD}$ rocking	861	0.63	
804		ν_{11} out-of-plane	803	$\sim \text{Dp}$	
722	<i>a'</i>	$\nu_8: \nu (\text{C}-\text{Cl})$	697	0.36	
714					
702	<i>a''</i>				
587		ν_{12} : torsional	590	Dp	
385	<i>a'</i>	$\nu_9 \delta (\text{C}=\text{C}-\text{Cl})$	393	0.57	
--					

*Fermi resonance; sh. shoulder.

TABLE III
TELLER-REDLICH PRODUCT RULE RATIOS
FOR $\text{CH}_2=\text{CHCl}$ AND $\text{CH}_2=\text{CDCl}$

Species	<i>a'</i>	<i>a''</i>
Observed ratio	0.518	0.812
Theoretical ratio	0.516	0.807

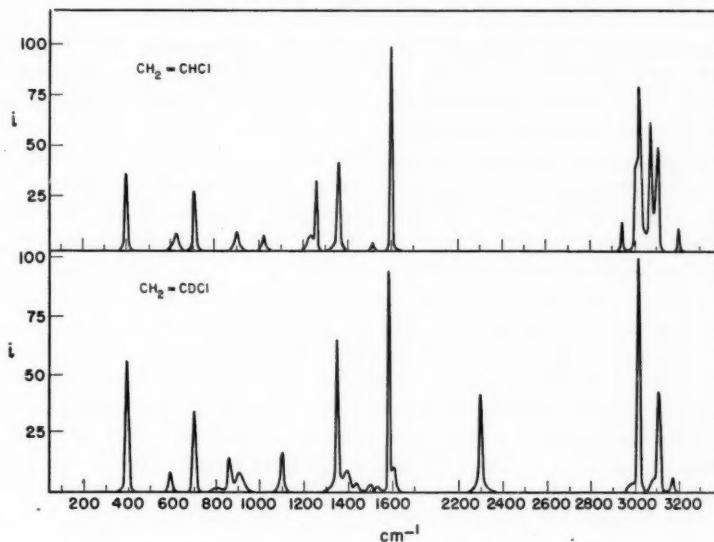


FIG. 1. Raman spectra of $\text{CH}_2=\text{CHCl}$ and $\text{CH}_2=\text{CDCl}$ in the liquid state. Temp. -100°C . $\pm 5^\circ\text{C}$. Volume of sample 6 ml. Slit widths: $\sim 7.5 \text{ cm}^{-1}$ between 300 and 1600 cm^{-1} ; $\sim 6.5 \text{ cm}^{-1}$ in 3000 cm^{-1} region. The scales are different in the two spectra. In each case the band with highest peak is 100.

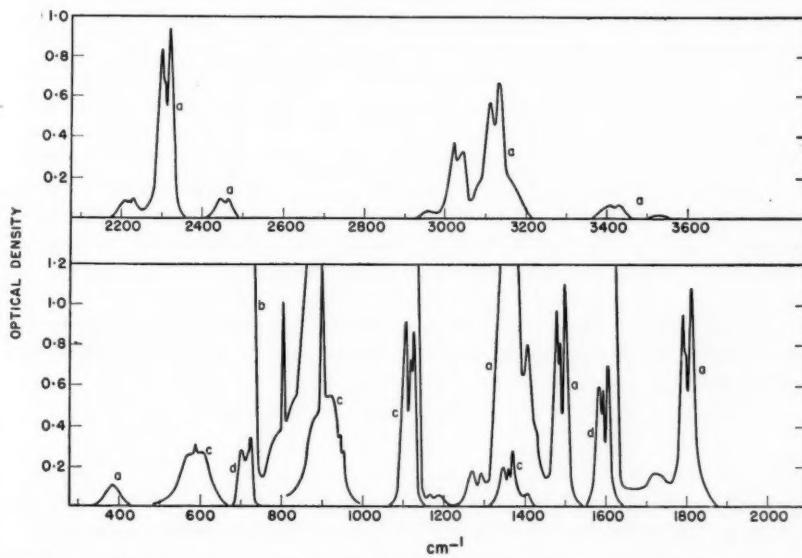


FIG. 2. Infrared spectrum of $\text{CH}_2=\text{CDCl}$ in the vapor state. 10 cm. cell at 20°C . Vapor pressures: *a*, 760 mm.; *b*, 370 mm.; *c*, 75 mm.; *d*, 19 mm. Slit widths: 8, 3, 3, 4, 3, 3, and 2 cm^{-1} in the regions 3000 , 2000 , 1600 , 1300 , 1000 , 700 , and 400 cm^{-1} respectively.

DISCUSSION

Both molecules have the same symmetry, Cs, (5) and all twelve modes of each should be infrared and Raman active. The nine planar modes, species a' , and the three out-of-plane modes, species a'' , should give rise to polarized and depolarized Raman bands respectively.

Little need be said about the Raman spectrum of $\text{CH}_2=\text{CHCl}$. The depolarization ratios confirmed the assignment, based on the observed envelopes of the infrared bands of the vapor, which was made by Thompson and Torkington (8). The a'' mode at 942.5 cm^{-1} in the infrared was not observed in the Raman spectrum.

For $\text{CH}_2=\text{CDCl}$ the bands were readily separated into the a' and a'' species by means of the depolarization ratios in the Raman spectrum and the vapor band contours in the infrared. The molecule approximates to a symmetric rotator* with moments of inertia $C = 18.7$; and $A = B = 149 \times 10^{-40} \text{ gm. cm.}^2$. The a'' modes are essentially perpendicular modes and should give rise to infrared bands with strong central peaks. The three bands with such a structure correspond to three depolarized Raman bands. The PR separation calculated using Gerhard and Dennison's formula (4) for parallel bands of a symmetric rotator with moments of inertia of 18.7 and 149.5 is approximately 20 cm^{-1} . Most of the infrared bands have a triplet structure with two strong outer peaks separated by $\sim 20 \text{ cm}^{-1}$, and a very weak central peak. The fundamental modes were readily identified. One mode, the a' mode at 861 cm^{-1} in the Raman, was not observed in the infrared spectrum probably because it was obscured by the strong a'' band at 900 cm^{-1} .

The agreement between the theoretical and observed product rule ratios was satisfactory. The results are collected in Table III.

When a correlation of the fundamentals of $\text{CH}_2=\text{CHCl}$ and $\text{CH}_2=\text{CDCl}$ is attempted using the approximate descriptions of the modes given in Table I, it is apparent that an unexpected change has occurred. Two bands, that arising from the in-plane rocking mode of the CH group (1274 cm^{-1}) and that arising from the in-plane rocking mode of the CH_2 group (1026 cm^{-1}), have shown major changes upon deuterium substitution. The explanation for the large change ($>\sqrt{2}$) in the former band's position and the anomalous increase in frequency of the latter must presumably be looked for in the coupling, in $\text{CH}_2=\text{CDCl}$, of vibrational modes which, in $\text{CH}_2=\text{CHCl}$, are well separated, thus allowing only a small interaction. A closely similar situation occurs in the corresponding bromo compounds where the following tentative assignment was made (1):

	$\text{CH}_2=\text{CHBr}$	$\text{CH}_2=\text{CDBr}$
CH_2 rocking	1006	1091
CH, CD rocking	1256	841

More data are available for the bromo compounds where all the possible hydrogen-deuterium homologues of vinyl bromide have been examined (1).

*Using the dimensions (5): $C-\text{Cl} = 1.78 \text{ \AA}$, $C=C = 1.33 \text{ \AA}$, $C-H = 1.08 \text{ \AA}$, $C-C-\text{Cl} = 122^\circ$, $C-C-H = 120^\circ$, the moments of inertia were calculated to be:

$$I_A = 18.7, I_B = 140.2, I_C = 158.9 \times 10^{-40} \text{ gm. cm}^2$$

Comparison of the spectra of $\text{CD}_2=\text{CHBr}$ and $\text{CD}_2=\text{CDBr}$ shows that the CD rocking mode lies just below 1000 cm^{-1} . Deuterium substitution at the CH_2 group has only a relatively small effect upon the CH rocking mode as is shown by the band positions in $\text{CH}_2=\text{CHBr}$ (1256 cm^{-1}) and in $\text{CD}_2=\text{CHBr}$ (1239 cm^{-1}). So it is not unreasonable to assume that the CH_2 rocking mode will also be relatively unaffected by deuterium substitution at the other carbon atom. On this basis, both the CH_2 rocking and the CD rocking modes in $\text{CH}_2=\text{CDBr}$ would be expected near 1000 cm^{-1} . It is probable that strong coupling of the modes occurs, giving rise to two new vibrational levels at 841 cm^{-1} and 1091 cm^{-1} . These modes cannot therefore be described simply as CH_2 rocking and CD rocking.

For the two vinyl chlorides the argument is the same; only the band positions differ. The remaining a' modes in the two molecules may readily be correlated in accordance with the approximate descriptions in Table I.

One of the a'' modes, the torsional mode, is easily identified in both molecules but the correlation of the other two out-of-plane modes is uncertain. In $\text{CH}_2=\text{CHCl}$ they are about 40 cm^{-1} apart while in $\text{CH}_2=\text{CDCl}$ the separation is increased to about 100 cm^{-1} .

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THE MESOMORPHIC BEHAVIOR OF ANHYDROUS SOAPS

PART II. DENSITIES OF ALKALI METAL STEARATES¹

By D. P. BENTON,² P. G. HOWE,² R. FARNAND, AND I. E. PUDDINGTON

ABSTRACT

The densities of the series of alkali metal stearates and of a number of sodium stearates having substituents in the hydrocarbon chain have been measured over a temperature range of 25–380°C. Discontinuities in the density-temperature relationships indicate the transitions between the various mesomorphic forms in which these soaps exist and the results are compared with transition data obtained by an optical method, described in Part I of this series. Mesomorphism is found to be much less pronounced in the substituted stearates examined than in the normal soaps.

INTRODUCTION

In the extensive and varied studies that have been made of the mesomorphic behavior of salts of the long chain fatty acids, dilatometric measurements have been found particularly useful, since many of the thermal transformations between successive phases are accompanied by conspicuous changes in specific volume (2, 4, 5, 7, 8).

This paper presents the results of a study of the density-temperature relationships of the series of alkali metal stearates and of a number of sodium stearates having substituents in the hydrocarbon chain. The work parallels the previously reported transition data, obtained by an optical method, for the same soaps (1). To facilitate comparison of the data for the different soaps and for use in connection with electrical conductivity and viscosity data, to be presented in subsequent papers in this series, the density measurements have been made on an absolute basis.

EXPERIMENTAL

The sources of materials and methods of preparation of the soaps used in this work were as described previously (1). J-shaped, weight dilatometers were used. A weighed quantity of soap, previously fused under vacuum to remove last traces of water and alcohol (1), was introduced to the dilatometer before sealing to the capillary. The apparatus was then evacuated to a pressure not exceeding 10^{-8} mm. Hg, at a temperature above the final melting point of the soap and, after cooling, mercury was admitted to fill the dilatometer. A 2 meter length of 0.5 mm. diam. capillary was sealed to the capillary outlet and the dilatometer was set in an air thermostat so that the long capillary protruded vertically. The thermostat consisted of heavily lagged, hollow dural block which was heated electrically and controlled by a well-distributed mercury regulator. Calibrated complete immersion thermometers were used within the air bath and temperature control was better than $\pm 0.5^\circ\text{C}$. over the range 25–355°C.

The upper ends of the capillaries were bent over and dipped below the

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²National Research Council Postdoctorate Fellow, 1953–55.

surface of mercury in small weighing bottles. The weights of mercury expelled from the dilatometers as the temperature was raised were determined at 5–10° intervals. Not more than two determinations were made per day, thus allowing a time found to ensure attainment of equilibrium values. The use of the 2 meter length of capillary gave a total pressure of about four atmospheres on a soap sample and appeared to prevent vacuole formation within the sample on cooling (6). Using this device, reproducible values of the weight of mercury expelled at a given temperature were obtained in every case on passing through the cycle of melting to isotropic liquid and cooling to room temperature.

After completion of the above measurements, the capillary was broken at the point of exit from the thermostat and the dilatometer, containing soap and mercury, was weighed. The dilatometer was then emptied, cleaned, and weighed and finally weighed when completely filled with mercury. The density of a soap at temperature T was calculated using the equation

$$\text{density of soap at temp. } T = W_s/[W_0/\rho_t - (W_M - W_T)/\rho_T]$$

where W_s = weight of soap, W_0 = weight of mercury required to fill dilatometer at temperature t , W_M = weight of mercury in dilatometer with soap at temperature t , W_T = weight of mercury expelled at temperature T ($W_T = 0$ when $t = T$), ρ_t and ρ_T = densities of mercury at t and T . The assumptions thus made are that the expansion of the glass dilatometer and the expansion of the small quantity of mercury in the capillary outside the thermostat are negligible.

In order to check the accuracy of the absolute density values, some subsidiary measurements were made in the higher temperature regions, by means of a different experimental method. A small glass bulb, of approximately 0.25 ml. capacity, was formed at the end of a uniform, calibrated 2 mm. capillary and the bulb calibrated. This container was baked out at 380°C. under vacuum, let down under dry nitrogen, and the required amount of soap weighed in. The apparatus was evacuated, the soap melted, and dry nitrogen introduced into the tube above the soap. An amount of soap was used so that, at about the melting point, the meniscus lay somewhere near the center of the capillary. The apparatus was mounted in a dural block furnace, fitted with a glass covered viewing slot. The slot was illuminated at one side and readings of the height of the meniscus made with a telescopic cathetometer through the other, after equilibration at various temperatures. An etched ring on the capillary tube, used for the volume calibration, was used as a reference point for readings. Measurements below the final melting points of the soaps could only be made in some cases where the soap-glass adhesion was sufficiently low. However, this method provided a check on the values obtained at the highest temperatures with the mercury dilatometers and allowed observations to be extended to about 380°C.

RESULTS AND DISCUSSION

Results for the series of alkali metal stearates are shown graphically in Fig. 1. The curve for lithium stearate shows only three transitions, at 229°, 176°, and

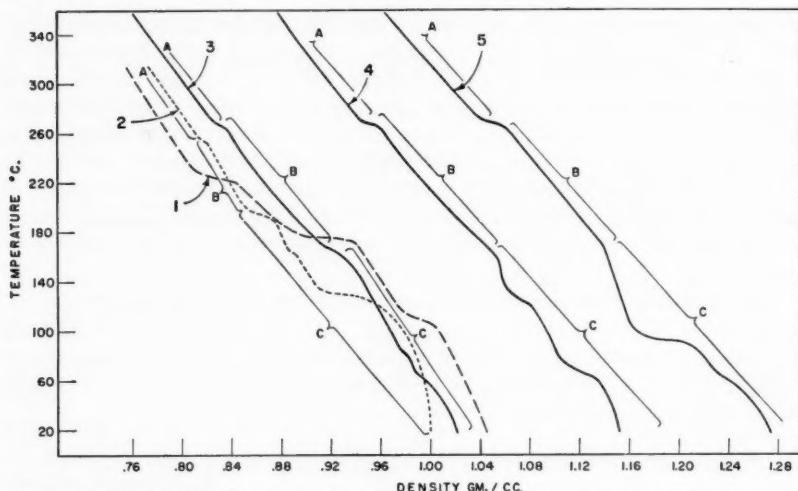


FIG. 1. Densities of alkali metal stearates. 1. Lithium stearate. 2. Sodium stearate. 3. Potassium stearate. 4. Rubidium stearate. 5. Cesium stearate.

115°C. This is similar to the behavior of lithium palmitate (8), which exhibits transitions at 223°, 190°, and 103°C. Supercooling occurred at the final melting point, cf. Part I (1).

The density-temperature curves for the four other alkali metal stearates may each be divided into three major portions, viz., the linear region A, the second linear region B, and the remaining region C.

(1) The linear region A. These regions contain the neat phase and isotropic liquid in each case. The temperatures at the terminations of regions A agree closely with the subneat-neat transition temperatures for the four soaps, determined by the optical method (1). The final melting points of these four soaps are not manifested by sufficiently substantial discontinuities in the density-temperature relationships to produce noticeable deviations from linearity in the graphs.

(2) The linear region B. The next break in the curve for sodium stearate occurs at 190–200°C. This is doubtless a manifestation of the transition which caused a major discontinuity in the light transmission-temperature curve for this soap at 188°C. (1) and ascribed to the change from the subneat to the superwaxy phase. The corresponding terminations of the linear regions in potassium, rubidium, and cesium stearates occur at 160–165°C., 160°C., and about 170°C. respectively. It is noteworthy that these are close to the temperatures at which these soaps were found to become opaque (1). It is suggested that these changes indicate transitions in potassium, rubidium, and cesium stearates corresponding to the subneat-superwaxy transition in sodium stearate.

The regions B would thus represent the subneat phases of this series of soaps. We may note that the optical studies (1) indicated minor transitions within

the subneat phases at 220°, 242°, and 222°C. for sodium, potassium, and rubidium stearates respectively. However, it would appear from dilatometric measurements that no radical changes in molecular packing occur within this region.

(3) The region C. The curve, in region C, for sodium stearate is seen to show an irregularity at about 165°C., corresponding to the discontinuity found by light transmission (1) at this temperature. At 132°C., the temperature ascribed to the transition waxy-subwaxy soap (7), a large density change commences and proceeds in an apparently continuous manner to that of the room temperature crystalline soap. The continuous nature of the density-temperature relationship for sodium stearate in this range, 25–132°C., has been observed previously (2, 6) in spite of very considerable precautions to ensure attainment of equilibrium values, although it has been shown by differential thermal analysis (7) that at least two thermal transitions, at approximately 90° and 117°C., do in fact occur.

The curves in region C for potassium, rubidium, and cesium stearates are seen to be basically of similar form to that for sodium stearate. However, by consideration of the property of density alone, a choice of possible interpretation into corresponding phases is afforded. The lowest temperature regions at 25–70°C., 25–75°C., and 25–70°C., in the curves for potassium, rubidium, and cesium stearates respectively, may correspond to the 25–132°C. region for sodium stearate. In this case the discontinuities at 90°, 130°, and 100°C. presumably would correspond to that at 165°C. in sodium stearate. On the other hand, the regions 25–90°, 25–130°, and 25–100°C. in potassium, rubidium, and cesium stearates may correspond, as a whole, to the 25–132°C. region in sodium stearate. If this is the case, then discontinuities within these regions might correspond to the transitions in sodium stearate that become apparent by reason of their heats of transition.

Consideration of the behavior of the soaps in dispersion in oil is of interest in this connection. The transition at 117°C. in sodium stearate is close to the temperature at which an unsheared dispersion in oil, of this soap, precipitates soap on cooling from a higher temperature or, conversely, close to the swelling temperature of the soap in oil (3). Loosening of the interactions in the hydrocarbon tail-tail planes of the soap lattice is believed to be involved at this temperature. Although observation of the like phenomenon with potassium, rubidium, and cesium stearates is rendered more difficult, by virtue of the greater difficulty of their initial dispersion by application of heat alone, comparable precipitation of these soaps appears to occur at about 70°C. This observation would appear to favor the second of the alternative interpretations postulated above. However, X-ray studies in the temperature ranges in question may be desirable before a choice is made between the two interpretations.

To supplement the graphical presentation of the density data, the numerical values within some of the phase ranges are given in Table I. This table also shows the density values for the isotropic liquids determined by the supplementary experimental method. Agreement between results obtained by the two methods is within 0–2%.

TABLE I

Phase	Lithium stearate			Sodium stearate			Potassium stearate			Rubidium stearate			Cesium stearate		
	Temp.	Temp.	Density	Temp.	Temp.	Density	Temp.	Temp.	Density	Temp.	Temp.	Density	Temp.	Temp.	Density
Curd and waxy	25-100°	1.04-1.00	25-130°	1.00-0.93	25-165°	1.02-0.92	25-165°	1.15-1.05	25-90°	1.27-1.21					
	110-170°	1.00-0.94	135-190°	0.91-0.87						100-170°	1.17-1.14				
Subneat	180-220°	0.90-0.84	195-258°	0.86-0.82	165-265°	0.92-0.84	165-265°	1.05-0.96	170-270°	1.14-1.05					
Neat			260-283°	0.81-0.795	270-353°	0.83-0.77	270-357°	0.94-0.88	275-351°	1.04-0.97					
Isotropic liq.	229-310°	0.81-0.76	283-310°	0.795-0.78	*360-380°	0.78-0.77	*360-380°	0.885-0.87	*360-380°	0.99-0.97					
	*235-350°	0.82-0.75	*285-330°	0.80-0.77											

Numbers in italics are the limit of measurements with Hg dilatometers.

*Values obtained by supplementary experimental method.

The molecular volumes of the series of alkali metal stearates, as functions of temperature, are shown graphically in Fig. 2. It is seen that the magnitudes of

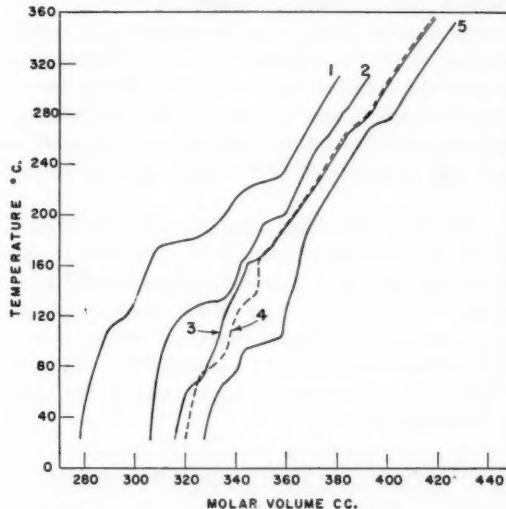


FIG. 2. Molecular volumes of alkali metal stearates. 1. Lithium stearate. 2. Sodium stearate. 3. Potassium stearate. 4. Rubidium stearate. 5. Cesium stearate.

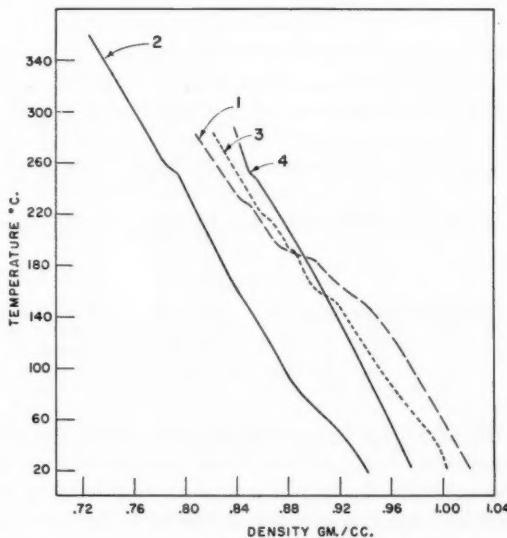


FIG. 3. Densities of substituted sodium stearates. 1. Sodium 12-hydroxy stearate. 2. Sodium 10-methyl stearate. 3. Sodium 9-keto 10-methyl stearate. 4. Sodium 9(10)-phenyl stearate.

this property increase from lithium stearate to cesium stearate, although the values for potassium and rubidium stearates in the subneat and neat phases and in the isotropic liquid are virtually identical.

Results of density determinations for the substituted sodium stearates are shown graphically in Fig. 3. It is apparent that the introduction of these substituent groups into the hydrocarbon chain of sodium stearate has greatly reduced the gross discontinuities in the density-temperature relationship. In the case of the phenyl stearate this relationship is virtually linear. A definite specific volume change is indicated at the final melting point, 250°C., of this soap.

The curves for sodium 9-CO-10-Me stearate and sodium 10-Me stearate also show only small departures from linearity. In the former case small discontinuities provide support for the minor transitions at 195° and 160°C. and the final melting point at 216°C. (1). The 10-Me stearate shows several slight deviations from a linear relationship at the lower temperature regions but the most conspicuous discontinuous specific volume change occurs at 255–260°C., in good agreement with the temperature at which this soap exhibited the major change in translucency (1).

The density-temperature curve for sodium 12-OH stearate is less linear than those for the other substituted soaps. Definite discontinuities occur at 185–195°C., and 225–230°C., again conforming with the results obtained by the light transmission technique (1).

Table II gives some numerical density data for the substituted stearates.

TABLE II

Soap	Temp.	Density
Sodium 10-Me stearate	25–255°	0.94–0.79
	265–355°	0.78–0.73
Sodium 9(10)-Ph stearate	25–245°	0.975–0.86
	255–280°	0.85–0.84
Sodium 9-CO-10-Me stearate	25–155°	1.005–0.915
	160–190°	0.90–0.885
	195–215°	0.88–0.87
	220–280°	0.86–0.825
Sodium 12-OH stearate	25–180°	1.20–0.905
	195–225°	0.875–0.855
	235–280°	0.84–0.81

Fig. 4 shows the molecular volumes of the substituted stearates plotted as a function of temperature. Progressive increase in molecular volume is exhibited as the size of the substituent group is increased. It is to be noted that the size of the substituent hydrocarbon group is indicated to be of primary importance in the effect on the nature of the crystal packing. Perhaps surprisingly, the further introduction of the polar keto grouping into the 10-methyl stearate does not substantially affect the molecular volume. Also, on comparing the

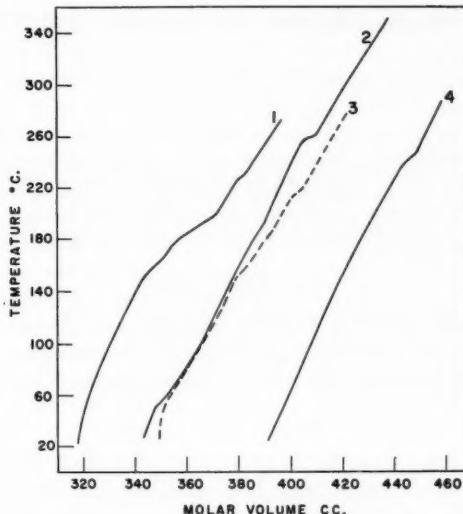


FIG. 4. Molecular volumes of substituted sodium stearates. 1. Sodium 12-hydroxy stearate. 2. Sodium 10-methyl stearate. 3. Sodium 9-keto 10-methyl stearate. 4. Sodium 9(10)-phenyl stearate.

molecular volume curves for sodium stearate and sodium 12-OH stearate, it is found that the effect of the polar hydroxyl group is less pronounced than that of the hydrocarbon substituents.

The density-temperature relationships of these substituted stearates indicate that the relative balance of polar and van der Waals interactions has been modified to a great degree and the stepwise structural changes of the normal soap, on heating, reduced in number or virtually eliminated. These substituted soaps appear to be very useful in grease preparation and likely to give lubricating materials with much more uniform behavior, over a range of operating temperatures, than those prepared with normal soaps.

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THE POLAROGRAPHY OF MALEIC HYDRAZIDE¹

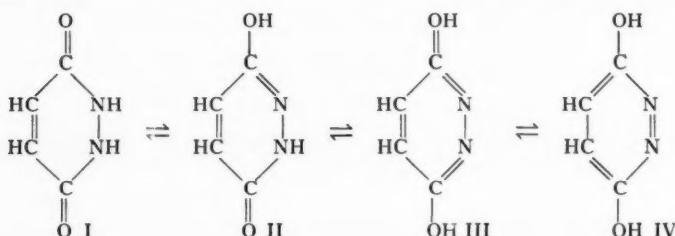
By D. M. MILLER

ABSTRACT

Maleic hydrazide was found to be similar to maleic acid in its polarographic behavior. Two pairs of double waves are produced, one in the region around pH 5.9 and the other around 8.2. The theory that the double waves are a result of the reduction of the undissociated acid followed by that of its anion at a higher negative potential appears to explain the first of these double waves but fails to explain the second.

INTRODUCTION

The polarographic behavior of maleic hydrazide (MH) was studied with the intention of using the polarographic method to follow some of the reactions of MH. It was also hoped that some information concerning the tautomeric



forms of MH might be obtained. The pyridazine ring in structures III and IV should make these forms highly aromatic with a possible similarity to hydroquinone. No anodic wave was found in the voltage range available to the dropping mercury electrode however, but a well-defined cathodic wave was produced. This cathodic wave is probably the result of the reduction of the carbon-carbon double bond of structure I. MH might then be expected to be polarographically analogous to maleic acid (MA), and since no information on the polarography of MH appears to have been published, reference will be made to the work on MA.

Elving and Teitelbaum (4) obtained waves for MA over the pH range of 0.7 to 12, and found a complicated relationship between E_1 and pH. A double wave occurred in the region of pH 5.9 but with increase in buffer concentration to one molar the two waves merged. The double wave was considered to be the result of insufficient buffering and all subsequent work was done at a buffer concentration of one molar. Elving and Rosenthal (3) reinvestigated MA using buffer concentrations ranging from 0.1 to 1.0 M and confirmed the existence of the double wave. These waves did not appear to be normal however, showing characteristics attributed to adsorption and kinetic control. A value of 4 was found for the polarographic constant $I_d = i_d/Cm^{2/3} t^{1/6}$ for the first wave

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in the pH range 0 to 4. As the pH increased beyond this range however I_d decreased reaching 0 at pH 6.5. I_d for the second wave increased as the first decreased, becoming equal to it at pH 6, and then passing through a maximum at pH 7 became 0 at pH 10. Similar results were found with fumaric acid.

Double waves having equal heights at pH 5.8 were reported for pyruvic acid by Müller and Baumberger (6), while Brdicka (1) showed that phenol-glyoxylic acid produced a double wave but its ethyl ester and ethyl pyruvate produced only single waves. This would indicate that the two waves are a result of the reduction of the free acid followed by the reduction of its anion at a more negative potential, a theory which received quantitative treatment by Brdicka and Wiesner (2) for monobasic acids and by Hanus and Brdicka (5) for dibasic acids. It was shown (2) that the pH at which the double waves are of equal height could occur several pH units higher than the pK_a for the acid, provided the formation of the free acid from its anion is fast enough.

EXPERIMENTAL

Polarograms were obtained with a Sargent Model XXI Recording Polarograph. Applied e.m.f. and pH measurements were made with a Beckman Model "G" pH meter. A saturated calomel electrode was used as reference in an H-cell maintained at $25 \pm 0.05^\circ\text{C}$. The resistance of all solutions was measured by an a-c. bridge and correction for *IR* drop applied where necessary. Reagent grade chemicals were used as supplied except for the MH which was recrystallized from water. All polarograms were obtained on solutions of $5.0 \times 10^{-4} M$ with respect to MH except where otherwise noted.

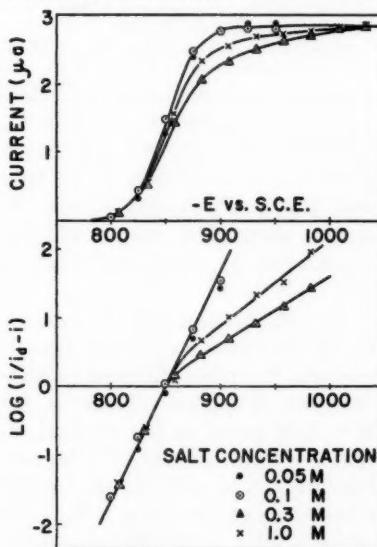


FIG. 1. Top: Polarographic curves of MH in $0.01 M$ HCl with KCl added to give indicated salt concentration ($-E$ in mv.).

Bottom: $\log i / (i_d - i)$ vs. $-E$ for above.

RESULTS

The effect of salt concentration on the polarographic waves was first investigated. Fig. 1 shows the results of increasing the salt concentration of a solution of MH in 0.01 *M* HCl (pH 2.19) from 0.05 *M* to 1.0 *M* using KCl. The top of Fig. 1 shows the polarograms and the bottom the $\log i/(i_d - i)$ vs. $-E$ plot. Both plainly show distortion at salt concentrations in excess of 0.1 *M*. Similar results were obtained with other buffer solutions whether KCl or the buffer itself was used to increase the salt concentration. In some cases $E_{\frac{1}{2}}$ was also found to be altered. As a result of these findings all subsequent polarograms were made on solutions of approximately 0.1 *M* with respect to the salt component. A list of the buffer systems used is given in Table I. Elving and

TABLE I
COMPONENTS AND APPROXIMATE CONCENTRATIONS OF BUFFERS

pH	Buffer system
1.21	0.1 <i>M</i> HCl
2.19	0.1 <i>M</i> KCl and 0.01 <i>M</i> HCl
3.50	0.1 <i>M</i> sodium formate and 0.1 <i>M</i> formic acid
4.89	0.05 <i>M</i> pyridine and 0.1 <i>M</i> pyridine hydrochloride
5.21	0.1 <i>M</i> pyridine and 0.1 <i>M</i> pyridine hydrochloride
5.51	0.1 <i>M</i> KH_2PO_4 and 0.005 <i>M</i> K_2HPO_4
5.80	0.1 <i>M</i> KH_2PO_4 and 0.01 <i>M</i> K_2HPO_4
6.15	0.1 <i>M</i> KH_2PO_4 and 0.02 <i>M</i> K_2HPO_4
6.85	0.1 <i>M</i> KH_2PO_4 and 0.1 <i>M</i> K_2HPO_4
7.40	0.1 <i>M</i> Triethanolamine (TEA) and 0.1 <i>M</i> TEA·HCl
7.87-8.88	0.1 <i>M</i> NH_4Cl titrated with NH_4OH
9.18	0.1 <i>M</i> NH_4Cl and 0.1 <i>M</i> NH_4OH
10.80	0.1 <i>M</i> K_2HPO_4 titrated with KOH
11.70	0.1 <i>M</i> KCl and 0.01 <i>M</i> KOH

Rosenthal (3) reported anomalous results from the use of acetate buffer and since similar difficulties were encountered in this work it was decided to avoid the use of acetate using pyridine in its place. The polarograms obtained for MH over the pH range 1.2 to 11.7 are shown in the top of Fig. 2. Three distinct waves are apparent. The first wave (I), existing at the lowest pH, exhibits a constant height up to about pH 5, beyond which it gradually decreases being replaced by a second wave (II) which is in turn replaced at higher pH by a third wave (III).

A plot of $\log i/(i_d - i)$ vs. $-E$ for each of these waves is shown in the lower section of Fig. 2. Where double waves occur, a separate plot is made for each wave. In all cases the straight line plots obtained indicate that the waves are of normal shape. One anomaly is apparent, however, in that the theoretical number of electrons ($n = 2$) involved in the electrode reaction, as obtained from the slope of these plots, is only realized in the lowest pH range. The slope of the remaining lines indicates a change to one electron (see column six, Table II) which must be fictitious since no reduction in I_d occurs simultaneously.

The half wave potentials ($-E_{\frac{1}{2}}$) and polarographic constants (I_d) of the three waves are given in Table II and plotted against pH in Fig. 3. The curves for I_d vs. pH (top of Fig. 3) show a striking similarity to those of Elving and Rosenthal for MA, the addition of the third wave (III) being the only essential

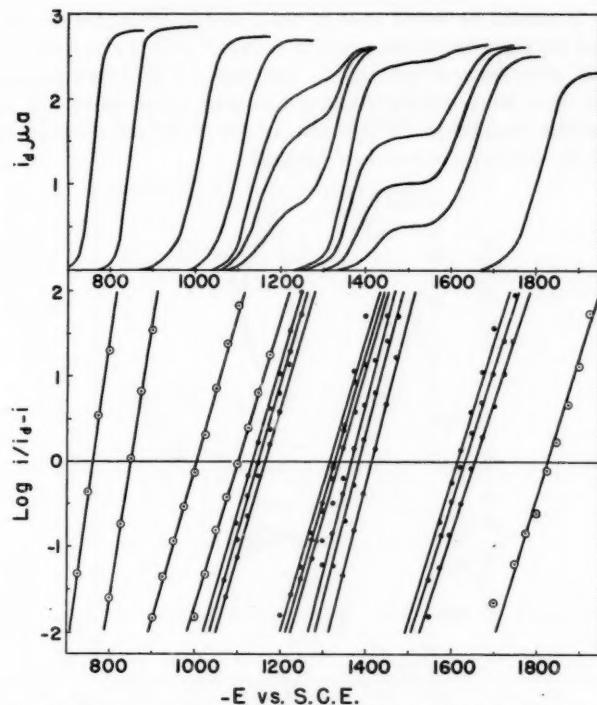


FIG. 2. Top: Polarographic curves of $5 \times 10^{-4} M$ MH at pH of 1.21, 2.19, 3.50, 4.89, 5.51, 5.80, 6.15, 6.85, 7.87, 8.38, 9.18, and 11.70 respectively ($-E$ in mv.).
 Bottom: $\log i/(i_d - i)$ vs. $-E$ for above.

TABLE II

pH	Wave	$-E_{1/2}$ vs. S.C.E., mv.	i_d , μA .	I_s	n
1.21	I	759	2.80	3.94	2.18
2.19	I	850	2.86	4.02	1.90
3.50	I	1002	2.75	3.85	1.07
4.89	I	1100	2.68	3.80	0.98
5.21	I	1125	2.60	3.68	1.09
5.51	I	1140	2.08	2.91	1.03
	II	1310	0.58	0.84	0.98
5.80	I	1152	1.60	2.28	1.05
	II	1325	1.00	1.44	1.09
6.21	I	1163	0.72	1.03	1.02
	II	1320	1.90	2.74	1.09
6.85	II	1356	2.42	3.48	1.05
7.40	II	1345	2.20	3.17	1.03
7.87	II	1368	1.57	2.28	1.18
	III	1615	1.06	1.57	1.02
8.38	II	1389	1.02	1.48	1.13
	III	1633	1.62	2.42	0.92
8.88	II	1410	0.66	0.96	1.20
	III	1648	1.94	2.90	0.92
9.18	II	1417	0.51	0.74	1.13
	III	1658	2.00	3.00	0.94
10.80	III	1780	2.40	3.58	0.83
11.70	III	1805	2.50	3.71	0.94

difference. It should be noted that in both cases curves start at I_d equal to 4 at pH 0 and that the crossover point of curves I and II occurs at pH 5.9. The $-E_{1/2}$ vs. pH plots for waves I and II (bottom of Fig. 3) are generally similar to those for MA. Both show a straight line portion for wave I at low pH but tend to become parallel to the pH axis as the crossover point is approached, while wave II appears more or less sigmoid.

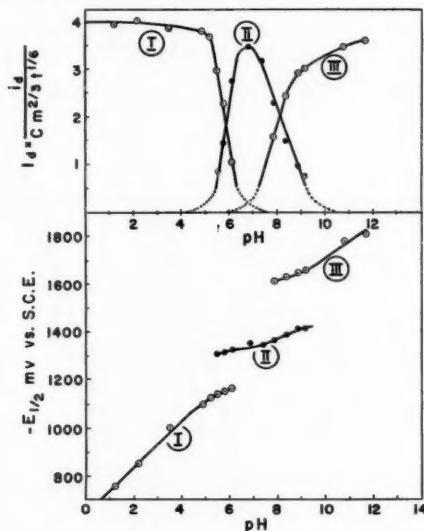


FIG. 3. Top: Polarographic constant I_d of MH vs. pH.
Bottom: Half wave potential of MH vs. pH.

The three curves for MH could be the result of the existence of three species. According to the theory of Brdicka *et al.* these species should be the free acid, its singly charged anion, and its doubly charged anion. There must therefore be two pK_a values for MH, the first being less than 5.9 (the first crossover point) and the second less than 8.2 (the second crossover point). An attempt to determine these by titration with NaOH gave a value of pK_{a1} equal to 5.67 but no value for pK_{a2} was found although the titration was carried to pH 12. The ultraviolet spectra of MH were then recorded at various pH values between 0.92 and 12.10. Two changes occurred with increasing pH as shown in Fig. 4. The height of the peak at $217 \text{ m}\mu$ (A in Fig. 4) increased and the position of the peak at $300 \text{ m}\mu$ shifted to $330 \text{ m}\mu$ (B in Fig. 4). These changes were plotted against pH in the usual way giving for pK_{a1} a value of 5.61 from A and 5.65 from B. No change in the spectra was noticeable from pH 7 to 12. Thus the second ionization constant, if it existed, must be greater than 12.

A test for the constancy of I_d with change in MH concentration was made and the values of I_d resulting are shown in Table III. For any given pH there appears to be little change in I_d for either waves I or II over the concentration range 0.5 to 2.0 mM.

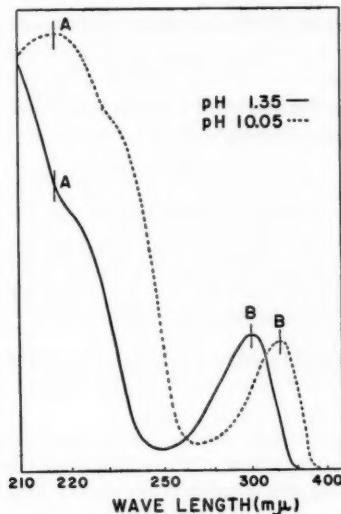


FIG. 4. Ultraviolet absorption curve for MH.

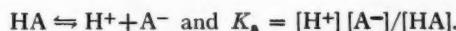
TABLE III

pH	Wave	MH, mM	i_s , μ a.	I_d
1.21	I	0.50	2.82	3.94
		1.00	5.58	3.94
		1.50	8.40	3.95
		2.00	11.7	4.12
5.80	I	0.50	1.60	2.28
		1.00	3.44	2.42
		1.50	5.40	2.54
		2.00	7.00	2.47
5.80	II	0.50	1.00	1.44
		1.00	1.90	1.34
		1.50	2.95	1.38
		2.00	3.85	1.36

DISCUSSION

The polarography of MH presents two main anomalies:

1. The apparent number of electrons (n) involved in the electrode process changes from two at low pH to one as the pH increases (Table II). This may be the result of a two step reduction, one step of which becomes irreversible as the pH increases.
2. Two sets of double waves are produced. The first of these may be explained using the concept of Brdicka *et al.* Treating MH as a monobasic acid HA, we may write:



The total concentration of MH is given by

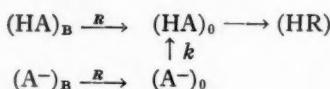
$$C = [HA]_B + [A^-]_B$$

where $[HA]_B$ and $[A^-]_B$ represent concentrations in the bulk of the solution. From these expressions it follows that

$$[1] \quad [HA]_B = C[H^+]/([H^+] + K_a),$$

$$[2] \quad [A^-]_B = C K_a / ([H^+] + K_a).$$

At potentials such that the diffusion current of the first wave alone has been reached, all HA molecules, but no A^- ions, arriving at the electrode are reduced immediately and the following processes occur:



where $(MA)_B$ and $(A^-)_B$ represent the species in the bulk of the solution and $(HA)_0$ and $(A^-)_0$ those at the electrode interface, R is the diffusion rate constant which is assumed to be approximately the same for HA and A^- , k is the rate constant for the association, and HR the reduced form of HA. In a well-buffered solution the hydrogen ion concentration can be assumed to be the same in the bulk and at the interface; thus if i_d is the diffusion current and Q a factor converting it to the proper units, the following steady state equations may be written:

$$[3] \quad d[HA]/dt = R[HA]_B + k[A^-]_0 [H^+] - Qi_d = 0,$$

$$[4] \quad d[A^-]/dt = R([A^-]_B - [A^-]_0) - k[A^-]_0 [H^+] = 0.$$

If i_d^0 is the diffusion current measured at large $[H^+]$ (i.e. $pH = 0$) so that $[A^-]_B$ is essentially 0, then

$$[5] \quad Qi_d^0 = RC.$$

From expressions [1] to [5] it can be shown that the ratio of the rate constants for association to that for diffusion is:

$$[6] \quad \frac{k}{R} = \frac{K_a[i_d^0/(i_d^0 - i_d)] - [H^+]}{[H^+]^2 + K_a[H^+]}.$$

Expression [6] may be checked by substituting $K_a = 2.24 \times 10^{-6}$ moles liters $^{-1}$, $i_d^0 = 2.83 \mu A$, and the appropriate values of i_d and $[H^+]$ into [6] to obtain k/R which should be constant over a wide range of hydrogen ion concentrations. The results obtained in this way follow:

$[H^+]$	k/R
$1.29 \times 10^{-6} M$	1.3×10^6 liters moles $^{-1}$
6.17×10^{-6}	2.6×10^6
3.09×10^{-6}	1.9×10^6
1.59×10^{-6}	2.2×10^6
6.17×10^{-7}	0.8×10^6

Although the ratio shows some variation, probably due to errors in pH measurements to which expression [6] is sensitive, there is no definite trend with change in pH; thus a value of 2×10^5 liters moles⁻¹ can be taken for k/R .

By substituting $i_d = \frac{1}{2}i_d^0$ into equation [6] the dependence of the hydrogen ion concentration at the crossover point ($[H^+]_{\frac{1}{2}}$) on the other factors is given by the expression

$$[7] \quad k/R = K_a - [H^+]_{\frac{1}{2}} / ([H^+]_{\frac{1}{2}}^2 + K_a[H^+]_{\frac{1}{2}}).$$

This equation is similar to the one obtained by Brdicka and Wiesner for similar conditions ($i_+ = i_-$ in their paper). It must be emphasized that since R is a complex function of diffusion and reaction rates, no absolute values of k can be obtained from the above form of the equation. It does give a fairly adequate qualitative picture, however, showing that the crossover point is not only a function of K_a but is dependent also on the relative rates of the diffusion and recombination processes.

On the basis of the above theory the second crossover point would occur when the reduction rate of the singly and doubly charged anions is equal. The second ionization constant, however, was found to be less than 10^{-12} , which is so much lower than $[H^+]_{\frac{1}{2}}$ that substitution in [7] would result in a negative value for k/R . This is of course meaningless, and the above theory must be discarded as an explanation of the second set of double waves. Elving and Teitelbaum (4) reported a double wave in the case of the diethyl esters of maleic and fumaric acids at a higher pH than for the acids themselves. This would indicate that the second set of waves cannot be attributed to normally ionized species but to some other pH dependent feature of the reduction. An explanation of these waves would most likely be found in a study of the mechanism of the electrode reaction. It would also seem advisable to reinvestigate the polarography of all acids giving a double wave, as well as their esters, under conditions similar to those used in this work, with the view to determining which compounds give a second set of double waves at higher pH. The methyl esters of MH are being investigated to this end.

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THE REACTION OF HYDROGEN ATOMS WITH METHYL CYANIDE¹

BY W. FORST² AND C. A. WINKLER

ABSTRACT

Hydrogen atoms produced in a discharge tube were found to react with methyl cyanide to produce hydrogen cyanide as the main product, together with smaller amounts of methane and ethane. The proposed mechanism involves the formation of hydrogen cyanide and a methyl radical in the initial step; methane and ethane are attributed to secondary reactions of the methyl radicals.

INTRODUCTION

The reaction of hydrogen atoms with methyl cyanide seems never to have been studied. A limited investigation of it has been made, partly for its intrinsic interest, and partly to provide information about the possible significance of hydrogen atom reactions during the reaction of active nitrogen with methyl cyanide, which will be reported in a later communication.

EXPERIMENTAL

The apparatus was essentially identical with that used for active nitrogen studies in this laboratory (1, 5) except for the methyl cyanide feed system. Methyl cyanide was stored as a liquid in a wide flat-bottomed bulb immersed in a thermostat regulated at $20.25 \pm 0.05^\circ\text{C}$., and the vapor drawn directly from the liquid surface. The methyl cyanide flow rate was varied by placing jets of different sizes in a flowmeter.

The molecular hydrogen flow rate was 7.95×10^{-5} mole/sec., corresponding to an operating pressure of 0.95 mm. Hg in the system.

Methyl cyanide, "chemically pure", was purchased from Brickman and Company and thoroughly dehydrated by one distillation over calcium chloride, followed by six distillations over P_2O_5 (13), and a final distillation over freshly fused potassium carbonate (9).

The condensable products of the reaction were distilled into a low temperature still of the type described by LeRoy (8). The C_2 fraction was distilled off at -140°C . and by mass-spectrometric analysis* was found to contain only ethane. The remainder of the products were distilled into an absorber containing $N/2$ KOH immersed in liquid air. After the solution had melted, the cyanide was determined by titration with silver nitrate (6). Three experiments were made in which the products were analyzed for cyanogen by the method due to Rhodes (11); the result in each case was negative. Samples of non-condensable products were withdrawn from the hydrogen stream by a Toepler pump and analyzed on the mass spectrometer. They contained only methane,

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in addition to excess hydrogen. There were traces of a white solid on the walls of the tube leading from the reaction vessel into the first trap.

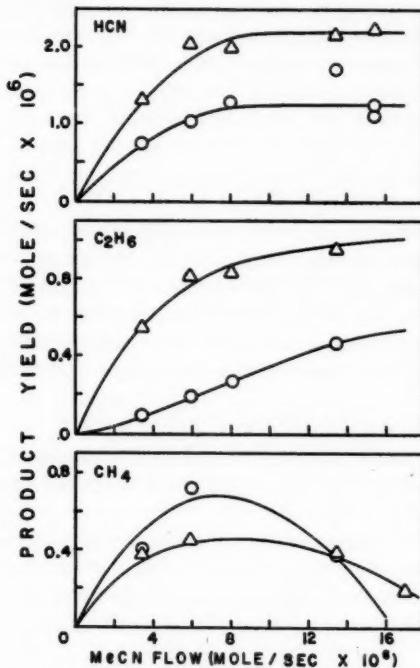
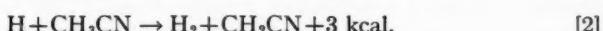


FIG. 1. Yields of hydrogen cyanide, ethane, and methane as functions of methyl cyanide flow rate.
Circles: 107°C. Triangles: 237°C.

The yields of hydrogen cyanide, ethane, and methane at 107° and 237°C. are plotted in Fig. 1 as functions of the methyl cyanide flow rate.

DISCUSSION

The initial attack of a hydrogen atom on the methyl cyanide molecule can be represented in three ways:



The heats of reaction in each case were calculated from heats of formation given in Reference (10). The heat of formation of the CH₂CN radical was estimated at about -70 kcal., and the heat of formation of the CN radical was taken as -93 kcal. (2, 10).

If reaction [1] occurs to an appreciable extent, some of the cyanide radicals formed in [1] should, at least at low MeCN flow rates, recombine to cyanogen. Since HCN but no cyanogen was found, every cyanide radical formed in [1] would have to be removed quantitatively by reactions leading ultimately to hydrogen cyanide. Moreover, with reaction [1] as initial step, there should be one molecule of methane produced for every cyanide radical disappearing. Fig. 1 shows that no such relation exists between the formation of HCN and CH₄. It would also be difficult to account for the presence of ethane in the products on this basis. Hence reaction [1] must be ruled out as a possible primary step.

If reaction [2] is the initial step, it is difficult to visualize how methane, ethane, and hydrogen cyanide could arise by further reactions of the cyano-methyl radicals produced. While it is true that recombination of the CH₂CN radicals to succinonitrile would account for the white deposit observed on the walls of the reaction vessel, this cannot be taken as proof that reaction [2] occurs, since CH₂CN radicals may also be formed in the reaction



which is known to occur (12). While reaction [2] does not appear to be attractive for the primary step, the present experiments do not permit its importance to be assessed directly.

If reactions [1] and [2] are considered unimportant, and the primary step is assumed to be reaction [3], methane and ethane would have to arise by subsequent reactions of methyl radicals, and at any flow rate of methyl cyanide the following relation between the products of the reaction should exist:

$$2(\text{moles of ethane}) + (\text{moles of methane}) = (\text{moles of HCN}).$$

Inspection of Fig. 1 shows that this is approximately true, within the relatively large experimental error. This agreement may, perhaps, be taken as evidence that, compared with reaction [3], reaction [2] does not occur to an appreciable extent.

The two curves in Fig. 1 representing the production of hydrogen cyanide as a function of methyl cyanide flow rate show that above a flow rate of about 8×10^{-6} mole/sec. MeCN, further increase in MeCN flow rate does not increase the production of hydrogen cyanide. A reasonable explanation of this behavior seems to be that the available supply of hydrogen atoms becomes exhausted.

If the flat portion of each curve represents complete consumption of all the available hydrogen atoms, there is reason to expect that the plateau should be higher at the lower temperature, since presumably more hydrogen atoms should be available at the lower temperature owing to a decreased number of collisions (in the gas phase and at the wall) leading to their recombination. From the relative positions of the two plateaus in Fig. 1, the experimental results seem to imply that the opposite is true. On the basis of a detailed mathematical treatment, it will be shown in a later communication that the change of plateau values with temperature could be accounted for on the assumption that

methyl cyanide acts as an efficient third body in the recombination of hydrogen atoms.

There are four obvious possibilities for secondary reactions of methyl radicals:



Reactions [4] and [5] have low activation energies, and both probably require a third body. Reactions [6] and [7] are both known to have activation energies of the order of 10 kcal. (14, 15). On the basis of this information, reactions [4] and [5] should be equally likely at 107°C. and 237°C., with reactions [6] and [7] becoming important only at the higher temperature. This conclusion appears to be borne out by the pattern of methane production shown in Fig. 1. At 107°C. the amount of methane formed rises with increasing methyl cyanide flow rate up to a maximum which corresponds roughly to the point where complete consumption of hydrogen atoms occurs, and then drops off sharply as the methyl cyanide flow rate is increased further. This suggests a strong dependence of methane production on hydrogen atom supply, and consequently reaction [4] must be responsible for a major part of the methane produced at this temperature. At 237°C. the decrease of methane production at MeCN flow rates corresponding to complete consumption of hydrogen atoms is less pronounced than at 107°C., and this may be taken as evidence that at this temperature reactions [6] and [7]—in addition to reaction [4]—contribute significantly to the formation of methane, as expected.

It is difficult to assess the relative importance of reactions [6] and [7]. It will be noted however that in reaction [6] a hydrogen atom is formed for each molecule of methane produced. If reaction [6] were the only important methane-producing step at high MeCN flow rates, a chain reaction could conceivably be set up in conjunction with reaction [3], resulting in continued increase of hydrogen cyanide yield at high MeCN flow rates. Since the hydrogen cyanide production curve (Fig. 1) reaches a flat plateau (within experimental error), it is very improbable that at high flow rates appreciable amounts of methane are produced in reaction [6].

There can be little doubt that ethane is due to recombination of methyl radicals, and by reference to the discussion of methane production the only other important reaction competing at both temperatures for methyl radicals at low MeCN flow rates should be reaction [4]. The fact that production of ethane increases markedly with a rise in temperature would then seem to be a matter of methyl radical concentration. The increased amount of reaction at 237°C. increases $[\text{CH}_3]$ relative to its value at 107°C., and this should profoundly affect the rate of formation of ethane, which depends on the second power of $[\text{CH}_3]$. The rate of formation of methane (reaction [4]) should also increase, though to a lesser extent.

Actually, a decline in the yield of methane is observed at 237°C., and this appears to be attributable to a decrease in hydrogen atom concentration. At low MeCN flow rates, only relatively few hydrogen atoms are removed in reactions [3] and [4], and in third order recombination with methyl cyanide as the third body. As a result, under these conditions, an appreciable part of the hydrogen atoms will recombine by H-H₂ collisions and at the wall, and, as mentioned, such recombination can be expected to exhibit a positive temperature coefficient. It appears that at 237°C. this hydrogen atom recombination is much more pronounced than at 107°C., to the extent that it may offset the effect of the temperature increase on [CH₃], hence on the rate of formation of methane, and lead to a reduced yield of methane at the higher temperature.

The reaction of hydrogen atoms with methyl cyanide appears to be essentially similar to the reactions of methyl halides with hydrogen atoms (3, 4, 7). This is perhaps not surprising since in many inorganic reactions the cyanide group exhibits a strong resemblance to the halogens.

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THE PREPARATION OF *o*- AND *p*-ACETAMINOBENZALdehydes¹

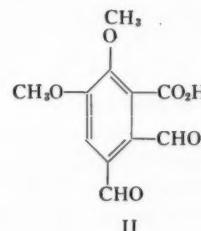
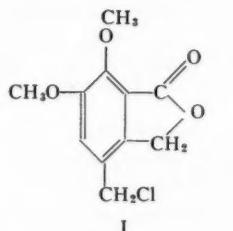
By J. J. BROWN² AND R. K. BROWN

ABSTRACT

Treatment of N,N-diacetyl-*o*-toluidine with N-bromosuccinimide followed by hydrolysis of the intermediate dibromo compound gave *o*-acetaminobenzaldehyde. The reaction was applied successfully to N,N-diacetyl-*p*-toluidine, N,N-diacetyl-4-chloro-*o*-toluidine, 2,4-bis(diacetamino)toluene, and 4-acetoxy-N,N-diacetyl-*o*-toluidine.

Both *o*- and *p*-acetaminobenzaldehyde were required for synthetic work in this laboratory. These compounds have been prepared in the usual way by the acetylation (6, 7) of *o*- and *p*-aminobenzaldehyde. However, the methods described in the literature for the preparation of *o*-aminobenzaldehyde by the reduction of *o*-nitrobenzaldehyde with ferrous sulphate and ammonia (15) and for *p*-aminobenzaldehyde by the action of sodium polysulphide upon *p*-nitrotoluene (3) are tedious, and the products must be used immediately in order to avoid self-condensation.

A direct preparation of *o*- and *p*-acetaminobenzaldehyde was suggested by the hydrolysis of N,N-diacetyl-*p*-toluidine (16) using aqueous sodium carbonate which gave a quantitative yield of *p*-acetotoluidide, and also by the work of Brown and Newbold (2) who used N-bromosuccinimide to oxidize 4-chloromethylmeconin(I) to 3-formylopanic acid (II).



We found that treatment of N,N-diacetyl-*p*-toluidine with two moles of N-bromosuccinimide in carbon tetrachloride, followed by aqueous sodium carbonate hydrolysis without isolation of the intermediate bromo compound, gave *p*-acetaminobenzaldehyde in 70% yield. Similarly, N,N-diacetyl-*o*-toluidine (16) gave *o*-acetaminobenzaldehyde in 66% yield.

The reaction was investigated further with respect to certain 4-substituted N,N-diacetyl-*o*-toluidines prepared by prolonged refluxing of the toluidine or its acetyl derivative in acetic anhydride. N,N-Diacetyl-4-chloro-*o*-toluidine, 2,4-bis(diacetamino)toluene, and 4-acetoxy-N,N-diacetyl-*o*-toluidine when

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treated with N-bromosuccinimide as above gave 2-acetamino-4-chlorobenzaldehyde (69%), 2,4-bis(acetamino)benzaldehyde (79%), and 2-acetamino-4-hydroxybenzaldehyde (70%) respectively.

The reaction was also applied to N,N-diacetyl-4-nitro-*o*-toluidine but the acetaminobenzaldehyde could not be isolated from the reaction mixture.

EXPERIMENTAL

Brominations using N-bromosuccinimide were carried out with irradiation from a Westinghouse Sunlamp (type R.S.-275 Watt) placed close to the flask.

p-Acetotoluidide

N,N-Diacetyl-*p*-toluidine (5 gm.) was treated with anhydrous sodium carbonate (10 gm.) and water (100 ml.) on the steam bath for one hour. Partial solution took place, and the solid which separated on cooling was crystallized from benzene to give *p*-acetotoluidide as blades, m.p. and mixed m.p. 149–150°.

p-Acetaminobenzaldehyde

A solution of N,N-diacetyl-*p*-toluidine (5 gm.) in carbon tetrachloride (100 ml.) containing 10.3 gm. of N-bromosuccinimide was heated under reflux on the steam bath for one hour. The filtered solution was evaporated under reduced pressure, and the residual red oil was heated with anhydrous sodium carbonate (10 gm.) in water (100 ml.) for one hour on the steam bath. The solution was decanted from a small amount of tar, extracted with ether (3×100 ml.), and the combined extracts were dried with sodium sulphate. Removal of solvent under reduced pressure gave a yellow solid which was crystallized from benzene – light petroleum (b.p. 30–60°) to give *p*-acetaminobenzaldehyde as needles (3 gm., 70%), m.p. 152–153° (lit.(7) 154.5–155°). Oxime, m.p. 206–207° (lit.(7) 205–206°). Calc. for C₉H₉O₂N: C, 66.2; H, 5.6. Found: C, 66.4; 5.5%.

o-Acetaminobenzaldehyde

N,N-Diacetyl-*o*-toluidine (5 gm.) was brominated as above, with the reflux time extended to eight hours. After hydrolysis of the product, the dried (Na₂SO₄) ethereal extract was evaporated to a dark red oil which was extracted thoroughly with boiling light petroleum (b.p. 30–60°). The extract was reduced to a small volume and placed in the refrigerator for one hour when *o*-acetaminobenzaldehyde separated as needles (2.8 gm., 66%), m.p. 68–70°. A specimen recrystallized from light petroleum (b.p. 30–60°) melted at 70–71° (lit. (6) 70–71°). Found: C, 66.6; H, 5.6%. Oxime, m.p. 193–194° (lit.(1) 194°).

N,N-Diacetyl-4-chloro-*o*-toluidine

4-Chloro-*o*-toluidine was prepared in good yield by the method of Hodgson and Moore (8). Twenty grams of 4-chloro-*o*-toluidine in acetic anhydride (50 ml.) was heated under reflux for 17 hr. The cooled solution was diluted with water (200 ml.) and the brown oil which separated was extracted with ether (3×50 ml.). The combined ethereal extracts were washed with water (2×50 ml.), 10% sodium bicarbonate solution (3×50 ml.), and water (50 ml.) and then dried (Na₂SO₄). The red oil obtained on removal of the solvent under reduced pressure was distilled to give N,N-diacetyl-4-chloro-*o*-toluidine as a

colorless oil which rapidly crystallized as needles (24 gm.), m.p. 40–42°, b.p. 154° at 8.5 mm. Calc. for $C_{11}H_{12}O_2NCl$: C, 58.5; H, 5.4. Found: C, 58.6; H, 5.6%.

2-Acetamino-4-chlorobenzaldehyde

N,N-Diacetyl-4-chloro-*o*-toluidine (5 gm.), N-bromosuccinimide (9 gm.), and carbon tetrachloride (100 ml.) were heated under reflux on the steam bath for three hours. The filtered solution when evaporated gave a yellow solid which was heated under reflux for 30 min. with a solution of anhydrous sodium carbonate (10 gm.) in water (50 ml.). The cooled reaction mixture was extracted with chloroform (3×50 ml.) and the combined chloroform extracts were dried (Na_2SO_4). Evaporation of solvent under reduced pressure, followed by crystallization of the yellow solid from aqueous ethanol, gave 2-acetamino-4-chlorobenzaldehyde as yellow blades (3 gm., 69%), m.p. 124–125°. Calc. for $C_9H_8O_2NCl$: C, 54.7; H, 4.1. Found: C, 54.7; H, 4.1%. The oxime crystallized from aqueous ethanol as needles, m.p. 215–216°. Calc. for $C_9H_9O_2N_2Cl$: C, 50.9; H, 4.3. Found: C, 50.8; H, 4.4%.

2-Acetamino-4-chlorobenzaldehyde was hydrolyzed to 2-amino-4-chlorobenzaldehyde by heating the former compound (1 gm.) with sodium hydroxide solution (40 ml., 2 *N*) and methanol (20 ml.) on the steam bath for 15 min. with occasional shaking. The solution was decanted from a small amount of tar, cooled, and extracted with ether (3×30 ml.). The combined ethereal extracts were washed with water (30 ml.), dried (Na_2SO_4), and evaporated to a yellow oil which soon solidified. Crystallization from aqueous ethanol gave 2-amino-4-chlorobenzaldehyde as needles (550 mgm.), m.p. 86–87°. Calc. for C_7H_6ONCl : C, 54.0; H, 3.9. Found: C, 53.8; H, 3.8%. Sachs and Sichel (14) give a melting point of 86° for the same compound obtained by reduction of 4-chloro-2-nitrobenzaldehyde using titanous chloride.

2,4-Bis(diacetamino)toluene

2,4-Bis(acetamino)toluene was prepared from 2,4-diaminotoluene (11) by the method of Lumière and Barbier (10). The compound melted at 219–223° (lit.(9) 223°). 2,4-Bis(acetamino)toluene (40 gm.) and acetic anhydride (200 ml.) were heated under reflux for 17 hr. The acetic anhydride was removed under reduced pressure and water (50 ml.) was added to the residue which was then extracted with chloroform (3×50 ml.). The combined chloroform extracts were washed with water (50 ml.), 10% sodium bicarbonate solution (50 ml.), and water (50 ml.) and then dried (Na_2SO_4). Removal of the solvent under reduced pressure gave a dark brown oil which solidified on standing. The solid, which was filtered with the aid of some ether and then washed with a small amount of ether, crystallized from benzene – light petroleum (b.p. 30–60°) to give 2,4-bis(diacetamino)toluene as prisms (20 gm.), m.p. 109–110°. Calc. for $C_{15}H_{18}O_4N_2$: C, 62.0; H, 6.25. Found: C, 62.2; H, 6.4%.

2,4-Bis(acetamino)benzaldehyde

2,4-Bis(diacetamino)toluene (5 gm.), N-bromosuccinimide (6.75 gm.), and carbon tetrachloride (100 ml.) were heated under reflux on the steam bath for

three hours. Evaporation of the solvent after filtration gave a yellow oil which was heated on the steam bath for 15 min. with a solution of anhydrous sodium carbonate (10 gm.) in water (50 ml.). The solid which separated on cooling was collected and crystallized from ethanol to give 2,4-bis(acetamino)benzaldehyde as plates (3 gm., 79%), m.p. 233–235°. Calc. for $C_{11}H_{12}O_3N_2$: C, 60.0; H, 5.5. Found: C, 59.8; H, 5.5%. Sachs and Kempf (13) give m.p. 235.5° for the compound obtained by treating the product of the ammonium sulphide reduction of 2,4-dinitrobenzaldehyde with acetic anhydride. The phenyl hydrazone melted at 252–254° (lit.(13) 246–252°).

2-Amino-p-cresol (Me = 1)

2-Nitro-*p*-toluidine, prepared in excellent yield by the method of Cohen and Dakin (4) for 4-nitro-*o*-toluidine, was converted into 2-nitro-*p*-cresol (17). Sodium dithionite (50 gm.) was added in small portions, with stirring, to 2-nitro-*p*-cresol (5 gm.) in a solution of potassium hydroxide (12 gm.) in water (100 ml.). After 15 min. at room temperature, the solution was acidified to Congo red with hydrochloric acid (d., 1.16) and heated on the steam bath to remove sulphur dioxide. The filtered solution was neutralized with 10% sodium bicarbonate, extracted with ether (4×100 ml.), and the combined ethereal extracts were washed with water (100 ml.) and dried (Na_2SO_4). Evaporation of solvent under reduced pressure yielded 2-amino-*p*-cresol as a brown solid (3 gm.), m.p. 147–150°. Copisarow (5) reports a melting point of 157–159° for the compound obtained by sodium sulphide reduction of 2-nitro-*p*-cresol.

4-Acetoxy-N,N-diacetyl-o-toluidine

2-Amino-*p*-cresol (5 gm.) and acetic anhydride (20 ml.) were heated under reflux for 17 hr. The cooled solution was diluted with water (100 ml.) and the product was isolated with ether as before. Removal of solvent gave a red oil which was extracted with boiling light petroleum (b.p. 30–60°). The solvent was reduced in volume and the remaining solution cooled in a refrigerator for one hour. The 4-acetoxy-*N,N*-diacetyl-*o*-toluidine separated as needles (4 gm.), m.p. 72–73°. Calc. for $C_{13}H_{16}O_4N$: C, 62.6; H, 6.1. Found: C, 62.4; H, 6.2%.

2-Acetamino-4-hydroxybenzaldehyde

4-Acetoxy-*N,N*-diacetyl-*o*-toluidine (2 gm.) and N-bromosuccinimide (3.15 gm.) in carbon tetrachloride (30 ml.) were heated under reflux for two and one-half hours on the steam bath. The yellow oil, obtained by evaporation of the filtered solvent, was heated on the steam bath for 30 min. with a solution of anhydrous sodium carbonate (4 gm.) in water (25 ml.). The solution was acidified with acetic acid and extracted with ether (5×50 ml.). The dried solution (Na_2SO_4), freed of solvent under reduced pressure, gave 2-acetamino-4-hydroxybenzaldehyde as a light brown solid. Crystallization from aqueous ethanol gave needles (1 gm., 70%) melting at 238–239°. Calc. for $C_9H_9O_3N$: C, 60.3; H, 5.1. Found: C, 60.2; H, 5.4%. The oxime crystallized from water as needles, m.p. 215° (decomp.). Calc. for $C_9H_{10}O_3N_2$: C, 55.7; H, 5.2. Found: C, 55.5; H, 5.5%.

N,N-Diacetyl-4-nitro-o-toluidine

4-Nitro-*o*-toluidine (20 gm.) (prepared according to Cohen and Dakin (4)) in acetic anhydride (50 ml.) was heated under reflux for 17 hr. The cooled solution was diluted with water (200 ml.) and the product, a dark red oil, was isolated with chloroform. The oil was dissolved in a few milliliters of benzene and the 4-nitro-*o*-acetotoluidide (5 gm.) which separated was filtered off, m.p. 151–153° (lit.(12) 150–151°). Evaporation of the filtrate gave a dark oil which soon solidified. Crystallization from benzene – light petroleum (b.p. 30–60°) gave N,N-diacetyl-4-nitro-*o*-toluidine as prisms (16 gm.), m.p. 81–83°. Calc. for C₁₁H₁₂O₄N₂: C, 55.9; H, 5.1. Found: C, 56.1; H, 5.2%.

ACKNOWLEDGMENT

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DEGRADATION OF D-GLUCOSE-1-C¹⁴ TO TRIOSE-REDUCTONE-C¹⁴¹

By H. F. BAUER AND CAROL TEED

ABSTRACT

Triose-reductone-C¹⁴ was obtained by treating D-glucose-1-C¹⁴ with sodium hydroxide in the presence of lead acetate at elevated temperatures. Carbon atoms four, five, and six, as well as carbon atoms one, two, and three, of the D-glucose molecule are shown to contribute to the triose-reductone yield. The formation of triose-reductone was found not to be accompanied by glycerol formation. Mechanisms for fragmentation of reducing sugars are discussed in the light of these findings.

INTRODUCTION

Triose-reductone, often called "glucoreductone" or "reductone", was discovered and isolated in a crystalline state by Euler and Martius (6) when they treated D-glucose with strong solutions of sodium hydroxide. It was subsequently shown that many reducing sugars yield triose-reductone under the same conditions but the methods for its isolation have been modified only slightly and D-glucose still remains the only practical source. By analogy with the ascorbic acids triose-reductone was assigned an α -carbonyl- α -enediol structure (I). This structure, though still widely accepted, cannot account for all of the observed properties of reductone and a resonance hybrid (II) has been suggested recently (12) as a more adequate alternative.

It was the object of this work to gain information about the mechanisms of decomposition of a hexose molecule to three-carbon fragments, especially triose-reductone, under the influence of alkali.

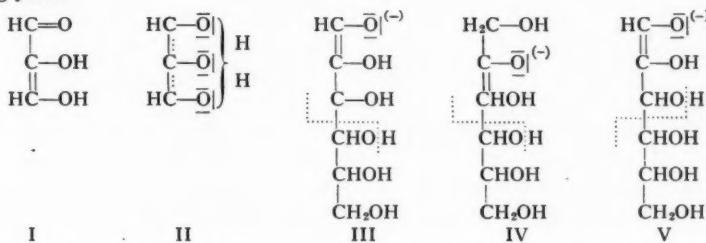
Two main mechanisms have been suggested for this disintegration. The older of these, postulated by Nef (10), involves an alkali-induced 1,2-enediol formation followed by a migration of the double bond via the 2- and 3-ketose to yield a 3,4-enediol. Fragmentation at the double bond was then assumed to result in the formation of two molecules of glyceraldehyde, which in turn could undergo a Lobry de Bruyn - Alberda van Ekenstein rearrangement to dihydroxyacetone or be enolized and oxidized to give triose-reductone. However, the step involving cleavage at the double bond has made this mechanism no longer acceptable since it was shown that the bond energy of a carbon-carbon double bond is much higher than of a single bond and that cleavage of a carbon chain occurs preferentially in α,β -position to a double bond (11, 14).

The other theory, first suggested by Evans and co-workers (1, 2), avoids the shortcomings of Nef's mechanism. Again a 1,2-enediolate ion (III) initiates the degradation reaction. The formation of triose-reductone and elucidation of its structure as an enediol have actually served as evidence for the existence of a 1,2-enediol (2) and other evidence can also be cited (7, 13), although the enediolic forms of the common reducing sugars themselves have never been

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isolated. The 2-ketose formed via the 1,2-enediolate can still undergo 2,3-enolization (IV) (16). The fragmentation to three-carbon fragments is then thought to occur by a reverse aldolization of the 1,2- or 2,3-enediolate between C-3 and C-4. The possibility of formation of a 3,4- and 4,5-enediolate to explain epimerizations observed on C-4 and C-5 is today regarded as very unlikely and the epimerizations are explained by a recombination of three-carbon fragments (18). A fragmentation as indicated in III and IV would lead to two molecules of triose, one being in an enolized form. Oxidation of the triose could then give rise to triose-reductone, a possibility that is suggested by the formation of triose-reductone by the action of alkali on dihydroxyacetone (17). According to Euler (3) a fragmentation as indicated by V would lead, however, directly from D-glucose to one molecule of triose-reductone and one molecule of glycerol.



The use of carbon-14 tracer techniques in recent studies of the action of alkali on carbohydrates (9, 15) has provided a deeper understanding of some aspects of the degradation reactions. It appeared, therefore, that preparation of triose-reductone from carbon-14 labelled sugars might likewise yield information suitable for evaluating the mechanisms discussed above. D-Glucose-1-C¹⁴ was dissolved in water and heated in a stream of nitrogen in the presence of lead acetate and small amounts of potassium cyanide (4, 6) and cupric acetate (5). Sodium hydroxide was then added and after the desired reaction time the mixture was neutralized with acetic acid. The triose-reductone lead salt was analyzed for its lead content and decomposed with the calculated amount of phosphoric acid. The purification was simplified and the yield of pure material increased by the finding that the triose-reductone obtained from the decomposition sublimes easily *in vacuo*. To determine the C¹⁴ content of the triose-reductone the compound was combusted to carbon dioxide, which was either analyzed as such in a gas phase counter, or counted as barium carbonate at infinite thickness in a gas flow counter (Table I).

TABLE I
CONTRIBUTION OF THE CARBON ATOMS OF D-GLUCOSE TO THE YIELD OF
TRIOSE-REDUCTONE

Activity in m μ c./mM. CO ₂		Contribution by	
D-Glucose-1-C ¹⁴	Triose-reductone-C ¹⁴	C-1+C-2+C-3	C-4+C-5+C-6
38.9	42.8	55.1%	44.9%
70.5	74.2	52.6%	47.4%

From the results of these analyses and by examining the mother liquors it could be shown that:

(a) Carbons 4, 5, and 6 of the D-glucose molecule as well as carbons 1, 2, and 3 contribute to the triose-reductone formation.

(b) The contribution of the bottom half of D-glucose to the yield of triose-reductone nearly equals that of the top half.

(c) No glycerol is formed from D-glucose in the degradation by alkali.

These findings strongly suggest that a fragmentation according to Euler (4) is not possible and that triose-reductone is a secondary reaction product derived from a three-carbon compound possibly by a fragmentation according to III and IV with triose-enediol as an intermediate. The small deficiency of triose-reductone formed from the bottom half of D-glucose might best be explained by the fact that the glyceraldehyde formed on the reverse aldolization has first to be converted to its enediolate before being oxidized to triose-reductone. Since enolization is not an instantaneous reaction (13), the top half of the molecule, already present as enediolate before fragmentation, is therefore converted to triose-reductone at a slightly faster rate. It was noted above that formation of triose-reductone has been taken as evidence for the existence of a 1,2-enediolate (III) in an alkaline solution of a hexose (2). However, since the compound is also derived from the bottom half of the molecule, its formation may not necessarily serve as a direct proof of this postulate.

EXPERIMENTAL

Triose-reductone-C¹⁴ from D-Glucose-1-C¹⁴

D-Glucose-1-C¹⁴, 25 gm., was dissolved in 375 ml. of water. Lead acetate, 13.5 gm., potassium cyanide, 3 mgm., and copper acetate (5), 50 mgm., were added and the solution was heated in a stream of nitrogen to 92°C. Sodium hydroxide, 8.5 gm. in 25 ml. of water, was added and the mixture was shaken for two to three minutes. It was then acidified with glacial acetic acid, 4 ml., and quickly cooled. The lead salt of triose-reductone-C¹⁴, 12.5 gm., was isolated by centrifuging, washed in succession with water, acetone, and ether, and dried *in vacuo*. The lead content of the salt was 58.8%. The lead salt was suspended in dry acetone, 50 ml., and phosphoric acid, 4.5 ml. of 85% acid, was added and the mixture was shaken for 30 min. at room temperature. The lead phosphate was filtered off and the acetone solution was concentrated *in vacuo* and cooled to -15°C. The crude crystals obtained on filtration were sublimed at 5 μ pressure and a bath temperature of 60-80°C. to yield 0.85 gm. of pure triose-reductone-C¹⁴, m.p. 153°C.

For determination of their radioactivity the samples of D-glucose-1-C¹⁴ and triose-reductone-C¹⁴ were combusted in an apparatus used for carbon-hydrogen microdeterminations. The carbon dioxide was converted to barium carbonate, which was plated by filtration on paper disks and counted at infinite thickness. A parallel determination was always carried out by combusting a sample with Van Slyke solution and measuring the activity of the carbon dioxide in a gas phase counter. The results obtained are listed in Table I.

In calculating the contribution of the different carbon atoms of D-glucose to the formation of triose-reductone, the following considerations were made: the maximum activity possible for triose-reductone is twice the activity of the hexose, and this value is attained through direct conversion of only carbons 1, 2, and 3 to reductone. In experiment 1, for example, the maximum theoretical value is 38.9×2 , or 77.8 m μ c./mM. CO₂. The activity of the derived reductone was 42.8 m μ c./mM. CO₂. Hence carbons 1, 2, and 3 of D-glucose contributed $(42.8/77.8) \times 100$, or 55.1% of the yield of the reductone. Dilution of the activity of the reductone from the maximum to the observed value was due, therefore, to the contribution of carbons 4, 5, and 6 (44.9%).

Large Scale Preparation of Triose-reductone

In general the preparation was carried out as described for the triose-reductone-C¹⁴. For the fragmentation of kilogram quantities of D-glucose it was advantageous to heat the solution by blowing in steam and to add the sodium hydroxide when the D-glucose solution had reached 87–88°C. Addition at higher temperatures was dangerous since the reaction mixture tended to boil vigorously. After neutralization the solution was cooled with crushed ice, 2–3 kgm., and the triose-reductone lead salt isolated by allowing it to settle and decanting the supernatant. The salt was washed in succession with water, acetone, and ether, always allowing the salt to settle and decanting the supernatant. This procedure required several hours but resulted in a purer lead salt since a cake obtained on filtration could not be washed efficiently. The crude triose-reductone isolated from the lead salt was sublimed in 20–30 gm. batches. One thousand grams of D-glucose yielded 32–35 gm. of pure triose-reductone.

Determination of Glycerol in the Reaction Mixture of D-Glucose with Alkali

D-Glucose, 25 gm., treated as described for D-glucose-1-C¹⁴, yielded a dark brown solution after the lead salt of triose-reductone was filtered off. This solution was concentrated *in vacuo* to a thin sirup and extracted continuously with ethyl acetate. The ethyl acetate extract and the original sirup were examined for the presence of glycerol (8). None could be detected. Addition of known amounts of glycerol to the sirup showed that the limit of identification (5 γ) and the limit of concentration (1:10,000) of glycerol was the same in the presence of sugars as in pure glycerol solutions.

ACKNOWLEDGMENT

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LIGHT ABSORPTION STUDIES

PART II. ULTRAVIOLET ABSORPTION SPECTRA OF SUBSTITUTED BENZOIC ACIDS AND PHENYL BENZOATES¹

BY W. F. FORBES AND M. B. SHERATTE

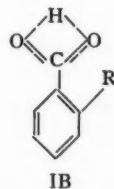
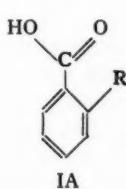
ABSTRACT

The spectra of a number of substituted benzoic acids, acetanilides, and phenyl benzoates are discussed in terms of the electronic and steric effects of substituents.

INTRODUCTION

The absorption band observed in the $230 \text{ m}\mu$ region of the absorption spectrum, and designated by Moser and Kohlenberg (12) as the B-band, is of interest in the *ortho*-substituted benzoic acids, since the usual explanation of the steric effect due to an *ortho*-substituent must be modified in order to account for the observed spectra.

The formula of benzoic acid may be written in two forms, one possessing an intact carboxyl group (type IA), the other a hydrogen-bridged structure (type IB). On steric considerations alone, neither form accounts satisfactorily



for all of the *ortho*-substituted benzoic acid spectra (see Table I). For example, supposing *o*-toluic acid exists as structure IA ($R = Me$), no unusual loss of intensity should be apparent since a similar conformation may be shown to be relatively insensitive to steric effects involving excited states only in *o*-methylacetophenone (8), where the OH group of IA is replaced by a methyl group. In *o*-toluic acid, however, there is observed a pronounced hypsochromic shift accompanied by almost complete loss of intensity of absorption as compared to *p*-toluic acid. Similarly, if IB ($R = Me$) alone were the correct configuration, and one *ortho*-methyl substituent was to produce a twist in the carbon-carbon linkage sufficient to accommodate the substituent, a second methyl substituent in the other *ortho*-position would not be expected to bring about much further change in the observed spectrum. However, in 2,6-dimethylbenzoic acid the band in this region has disappeared completely (12).

Hence it may be concluded that the observed changes in the B-band of the spectra of substituted benzoic acids are primarily due to the *electrical* effects of substituents, which is not unexpected since an isolated $C=O$ group is known

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Contribution from the Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland.

to be relatively small. Thus only very bulky substituents in the *ortho*-position would be expected to make steric overlap the primary factor in the observed changes of the spectra.

Electrical effects may be divided into *inductive* effects, and *mesomeric* (or resonance) effects. Bearing in mind the geometrically small hydroxyl group in benzoic acids, the *inductive* effect would be of greater importance in the *ortho*-position. Mesomeric effects are generally considered to be of equal importance in *ortho*- and *para*-positions. Of the substituents discussed here, methyl groups have a positive inductive effect (i.e. they repel electrons) while nitro, hydroxyl, and methoxyl groups, and halogens exert a negative inductive effect, the halogens being in the order F > Cl > Br > I. Only the nitro group exerts a negative mesomeric effect, while all the other groups referred to exert a positive mesomeric effect; the positive mesomeric effect of the halogens is in the order I > Br > Cl > F.

ULTRAVIOLET ABSORPTION SPECTRA

Para-substituted Benzoic Acids

Table I shows that all *para*-substituted benzoic acids, with the exception of *p*-nitrobenzoic acid, exhibit pronounced bathochromic shifts accompanied by enhanced intensity of absorption which are both approximately parallel to the *mesomeric* effect of the substituent, for example I > Br > Cl > F. The *inductive* effect in *para*-halogen compounds appears to be of secondary importance, since both the bathochromic shifts and the observed intensities of absorption may be correlated with the *mesomeric* effect, but not with the *inductive* effect of the substituent. In the above-mentioned example, the latter would suggest, in both bathochromic shifts and intensities, an order F > Cl > Br > I. In this connection the reported value of the absorption maximum for *p*-bromobenzoic acid (12), i.e. λ_{max} 240 m μ , $\epsilon = 12,500$, appeared to us to be slightly inaccurate with respect to the intensity at maximal absorption and a careful redetermination gave a value of $\epsilon = 16,000$ at 238.5 m μ , the wave-length of

TABLE I
ABSORPTION SPECTRA OF SUBSTITUTED BENZOIC ACIDS IN ABSOLUTE ETHANOL
Wave-lengths and intensities of the B-band maxima (values in italics represent inflections)

Acid	Position of substituent					
	Ortho		Meta		Para	
	λ_{max} , m μ	ϵ_{max}	λ_{max} , m μ	ϵ_{max}	λ_{max} , m μ	ϵ_{max}
Benzoic			(227	11000)		
Toluic* (12)	228	5000	232	9000	236	14,000
Fluorobenzoic	223	9500	225	10000	228	11,000
Chlorobenzoic* (12)	229	5000	230	8500	234	15,000
Bromobenzoic* (12)	224	6500	225	8500	238.5	16,000†
Iodobenzoic	233	7000	284	9500	252	17,000
Hydroxybenzoic* (12)	236	7500	236	6000	251	12,500
Anisic* (12)	230	6000	230	7000	249	14,000
Nitrobenzoic	~255	3500	255	7500	258	11,000

*Values in 95% ethanol.

†See experimental.

maximal absorption. This value of $\epsilon = 16,000$, as expected, lies between the values for the intensities at wave-length of maximal absorption of *p*-chlorobenzoic acid ($\epsilon = 15,000$) and *p*-iodobenzoic acid ($\epsilon = 17,000$) (see Table I).

p-Nitrobenzoic acid, because of the negative *mesomeric* effect of the nitro group, does not exhibit any enhanced intensity of absorption, and the spectrum resembles that of nitrobenzene itself (see below).

Meta-substituted Benzoic Acids

For *meta*-substituted benzoic acids, according to the above hypothesis, the *inductive* effect increases in importance, owing to the greater proximity of the heteroatoms and the more effective transmission of the electron release (or *mesomeric* effect) to the *ortho*- and *para*-positions. This will normally prevent the *mesomeric* effect of the substituent from making its contribution, and the molecular spectrum resembles that of the unsubstituted benzoic acid, but with a slightly decreased absorption intensity owing to the adverse *inductive* effect. Appreciable changes in the location of maximal absorption are observed only for *m*-ido- and *m*-nitro-benzoic acid, and this may be ascribed to the characteristic behavior of iodo atoms and nitro groups. In the iodobenzoic acids the interaction of the carboxyl group and the iodo atom is readily apparent. The *meta*-compound, compared to the *para*-compound, exhibits appreciable loss of intensity of absorption together with a pronounced change in the location of maximal absorption. This is of interest since in that region 2-iododiphenyl also exhibits a similar unusual absorption band—for a compound containing an iodophenyl group—which becomes apparent under conditions of slight steric strain (7). In the nitrobenzoic acids, the carboxyl groups, from an electrical point of view, appear to be of relatively little consequence. The spectrum of *p*-nitrobenzoic acid is altered as might have been expected from steric considerations, namely the *meta*-compound exhibits an hypsochromic shift accompanied by loss of intensity of absorption, and neither spectrum is radically different from that of nitrobenzene which was found to absorb maximally at 258 m μ , $\epsilon = 8500$. A fuller discussion of these effects, together with a semiquantitative examination of various theoretical formulas to account for these effects, will be the subject of a separate communication.

A similar explanation, that is in terms of steric factors, holds for the spectra of toluic acids, in which the *inductive* effect of the substituent is small. This steric effect becomes readily apparent in increasing magnitude *ortho* > *meta* > *para*. The increased sensitivity of benzoic acids to steric effects, compared with acetophenones, is ascribed to the more appreciable concentration of electrons in the excited state of the benzoic acid in the carboxyl group as compared with the acetyl group, and/or less double bond character in the carbon-carbon linkage. Thus the hindrance occurs chiefly in the excited state, which, as has previously been pointed out (8), explains the observation that the steric effect consists chiefly of decreased absorption intensity rather than of a pronounced hypsochromic shift of the band. The intermediate steric effect of the methyl group in the *meta*-position may be accounted for by the known but-

tressing effect of a methyl group in that position (3), that is the methyl group exerting a buttressing effect on the *ortho*-hydrogen atom which in turn sterically interacts with the carboxyl group.

The spectrum of benzoic acid may now also be correlated with other spectra in accordance with the above hypothesis. Benzoic acid absorbs maximally with smaller intensity of absorption than acetophenone and this may again be ascribed to steric inhibition of resonance in the excited state due to the *ortho*-hydrogen atoms. Both acetophenone and benzoic acid from dipole moment and X-ray crystallographic data (both of which measure ground state contributions only) appear to be planar, or nearly planar, in the ground state (4, 5, 14), which corroborates the postulated hindrance in the excited state. The steric hindrance in benzoic acid would therefore be expected to give rise to reduced absorption intensity and a slight hypsochromic shift. However, the ground state of benzoic acid is more stabilized by resonance forms than that of acetophenone, because the replacement of the methyl group in acetophenone, or the hydrogen atom in benzaldehyde, by the hydroxyl group of benzoic acid aids the setting up of polar excited states because of the negative *inductive* effect of the hydroxyl group; thus the energy level of the ground state of benzoic acid is reduced relative to that of acetophenone, and this together with the relative *increase* in the energy level of the excited state of benzoic acid with respect to acetophenone gives rise to a considerably greater energy difference in benzoic acid between the ground state and the excited state. Thus benzoic acid absorbs maximally at much shorter wave-length and lower intensity ($227 \text{ m}\mu, \epsilon = 11,000$) than either acetophenone ($240 \text{ m}\mu, \epsilon = 12,500$) or benzaldehyde ($244 \text{ m}\mu, \epsilon = 13,000$).

Ortho-substituted Benzoic Acids

Although as Moser and Kohlenberg (12) point out—from evidence involving comparisons with van der Waals radii—shifts in the wave-lengths of the B-band should not be assigned only to steric interference with coplanarity, the conclusion that the recorded values of maximal absorption of the *ortho*-substituted benzoic acids can best be rationalized by consideration of the steric factors involved appears to us irrefutable. Also van der Waals radii are rather unsatisfactory as a measure of intramolecular interference properties of atoms, particularly for groups containing heteroatoms whose electronegativity largely differs from that of the carbon atom. Heteroatoms may give rise to appreciable *mesomeric* and *inductive* effects, the latter especially affecting any semiquantitative interpretation of the values.

Toluic acids have already been discussed. It is supposed that both benzoic and *o*-toluic acid and possibly also 2,6-dimethylbenzoic acid are near-planar in the ground state, but the permitted planar or near-planar excited states are sharply reduced in the order benzoic acid > *ortho*-toluic acid > 2,6-dimethylbenzoic acid.

All the other above-mentioned *ortho*-substituted benzoic acids also show the expected hypsochromic shift of the absorption maxima accompanied by loss of intensity of absorption compared with the corresponding *para*-substituted compound.

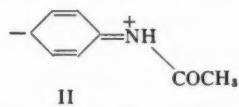
Acetanilides

Applying this hypothesis to the recently investigated ultraviolet absorption spectra of acetanilides (15; see Table II) it is seen that the data correspond with the generalizations made. Thus acetanilide itself, to which the steric

TABLE II
ABSORPTION SPECTRA OF SUBSTITUTED ACETANILIDES IN ABSOLUTE ETHANOL ACCORDING TO
UNGNADE (15)
Wave-lengths and intensities of the main maxima

Acetanilide	Position of substituent					
	Ortho		Meta		Para	
	λ_{\max} , $m\mu$	ϵ_{\max}	λ_{\max} , $m\mu$	ϵ_{\max}	λ_{\max} , $m\mu$	ϵ_{\max}
Acetanilide			(242	14,500)		
Methyl-	230	6500	245	14,000	245	15,000
Fluoro-	239	12500	242	15,100	240	13,000
Chloro-	240	10500	245	14,900	249	18,000
Bromo-	234	7500	246	14,000	252	18,500
Iodo-	Shoulder		246	13,500	254	23,000
Methoxy-	244	10500	245	11,500	249	15,000
Nitro-	233	17000	242	22,500	222	13,000

considerations referred to under benzoic acid do not apply, absorbs maximally in a similar manner to acetophenone, because of transitions involving polar excited states of type II (13). In *para*-substituted acetanilides, the shifts in the locations of maximal absorption and intensity changes again generally



correspond to the *mesomeric* effect of the substituents, for example I > Br > Cl > F. The *para*-nitro group gives rise to a pronounced hypsochromic shift because of the negative *mesomeric* effect of the nitro group and interaction with the NHCOCH_3 group (compare Table I for the spectrum of *p*-nitrobenzoic acid, where there appears to be no interaction).

For *meta*-substituted acetanilides, because of the *ortho-para* directive properties of the NHCOCH_3 group, that is its powerful electron-releasing properties, the spectra will even more resemble that of the unsubstituted acetanilide than was the case for *meta*-substituted benzoic acids. An exception is provided by the *m*-nitroacetanilide where the combination of a negative *inductive* effect together with the negative *mesomeric* effect of the nitro group appears to stabilize excited states of type II, thus giving rise to considerably increased intensity of absorption. Steric effects also become noticeable in some of the compounds, particularly where the substituent is large, such as in *m*-bromo- or *m*-iodo-acetanilide (see Table II). The nitroacetanilides as described above are of special interest. The negative *mesomeric* effect of the nitro group lessens the electron density of all ring carbon atoms, but the

ortho- and *para*-positions are deactivated almost exclusively, leaving the *meta*-position with the greatest concentration of electrons. Thus the *meta*-nitro compound exhibits the largest absorption intensity. It is tentatively proposed that in *o*-nitroacetanilide the steric hindrance of the *ortho*-substituents inhibits the deactivation mechanism and thus the spectrum of the *ortho*-compound reverts to a spectrum where the opposing *mesomeric* effect of the nitro group is less noticeable (see Table II).

In the other *ortho*-substituted acetanilides, steric effects play their expected part. This steric *ortho*-effect is generally strikingly similar to that observed in substituted benzoic acids and thus lends additional support to the proposed polar excited states of type II; comparison of Tables I and II indicates this, as for instance the halogen-substituted compounds, where the combination of *mesomeric*, *inductive* and steric effects gives rise to similar spectra. Discussing *ortho*-substituted acetanilides, Ungnade (15) states that there are no steric effects in *o*-methoxyacetanilide, but we believe that a steric effect hypothesis accounts more satisfactorily for the observed spectrum. Ungnade argues that although the primary band of *o*-methoxyacetanilide is somewhat less intense than that of the *meta*-isomer, the order of intensities is reversed for the secondary bands and the wave-lengths of corresponding bands in the *ortho*- and *meta*-isomers are virtually identical. In our view, the *ortho*-compound exhibits a typical steric effect of a type which has been discussed fully elsewhere (3, 4, 8), in which the location of maximal absorption remains approximately the same, while the intensity of absorption is reduced. This effect becomes readily apparent if the *ortho*-compound is compared with the corresponding *para*-compound rather than with the *meta*-compound. This seems justified, since it has been shown in the study of acetophenones (4, 8) that the former comparison has greater validity. We would propose a similar steric effect for the anisidine spectra referred to by Ungnade (15). Further, since it has been shown in a number of other examples (12, 8) that the secondary band is not apparently affected by steric interference of resonance, we would not expect the secondary band to exhibit a corresponding steric effect.

Aromatic Esters

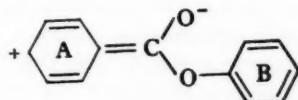
In the light of these hypotheses an examination of the spectra reported by Cilento (6) and the extension of this work to a number of other esters appeared to be of interest. The spectrum of phenyl benzoate we explain as follows: The spectrum of benzoic acid compared to acetophenone has been correlated by the *inductive* effect of the hydroxyl group and by consideration of steric factors operative largely in the excited state of benzoic acid. This steric effect in benzoic acid, postulated to be due to a concentration of electrons in the carboxyl group, is reduced somewhat in phenyl benzoate since the phenyl group attached to the oxygen atom (henceforth referred to as ring B in accordance with Cilento's nomenclature) is an electron-attracting group. It therefore removes some of the electrons responsible for the steric effect, and hence transitions to excited states of type III are aided, accounting for the increased intensity of absorption and the slight bathochromic shift. The value for the observed absorption intensity, however, also includes some absorption

TABLE III

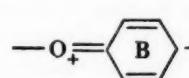
ABSORPTION SPECTRA OF AROMATIC ESTERS AND REFERENCE COMPOUNDS IN ABSOLUTE ETHANOL
Wave-lengths and intensities of the main maxima (values in italics represent inflections)

Compound	Substituent in:		Ring A band		Ring B band	
	Ring A	Ring B	$\lambda_{\max}, m\mu$	ϵ_{\max}	$\lambda_{\max}, m\mu$	ϵ_{\max}
(Benzoic acid)			(227	11,000)		
Phenyl benzoate	—	—	230	15,000	~274	2000
Phenyl <i>p</i> -chlorobenzoate	<i>p</i> -Chloro	—	242	20,000	—	—
Phenyl <i>p</i> -iodobenzoate	<i>p</i> -Iodo	—	259	21,000	—	—
Phenyl <i>p</i> -anisate (6)	<i>p</i> -Methoxy	—	261	22,000	—	—
Phenyl <i>p</i> -nitrobenzoate (6)	<i>p</i> -Nitro	—	259	15,500	~305	2500
<i>p</i> -Nitrophenyl <i>p</i> -anisate (6)	<i>p</i> -Methoxy	<i>p</i> -Nitro	276	27,400	—	—
<i>p</i> -Nitrophenyl <i>p</i> -nitrobenzoate (6)	<i>p</i> -Nitro	<i>p</i> -Nitro	266	20,600	—	—
<i>p</i> -Anisyl benzoate (6)	—	<i>p</i> -Methoxy	228	19,400	275	5000
<i>p</i> -Anisyl <i>p</i> -anisate (6)	<i>p</i> -Methoxy	<i>p</i> -Methoxy	261	23,500	—	—
<i>p</i> -Anisyl <i>p</i> -nitrobenzoate (6)	<i>p</i> -Nitro	<i>p</i> -Methoxy	258	15,500	~300	4000
<i>p</i> -Chlorophenyl <i>p</i> -chlorobenzoate	<i>p</i> -Chloro	<i>p</i> -Chloro	249	22,000	274	3000
<i>p</i> -Iodophenyl <i>p</i> -iodobenzoate	<i>p</i> -Iodo	<i>p</i> -Iodo	260	22,000	—	—
<i>m</i> -Anisyl benzoate	—	<i>m</i> -Methoxy	225	17,000	271	3500
<i>m</i> -Anisyl <i>p</i> -anisate	<i>p</i> -Methoxy	<i>m</i> -Methoxy	259	21,000	—	—
<i>m</i> -Anisyl <i>p</i> -nitrobenzoate	<i>p</i> -Nitro	<i>m</i> -Methoxy	256.5	20,000	~295	3000
<i>p</i> -Chlorophenyl benzoate	—	<i>p</i> -Chloro	232	17,500	~273	2500
<i>p</i> -Iodophenyl benzoate	—	<i>p</i> -Iodo	233	23,800	~270	4000
<i>p</i> -Nitrophenyl benzoate (6)	—	<i>p</i> -Nitro	235	14,100	270	14300
Cyclohexane ring						
Phenyl cyclohexane-carboxylate	—	—	—	—	258	2500
<i>p</i> -Nitrophenyl cyclohexanecarboxylate	—	<i>p</i> -Nitro	—	—	268	10000
<i>p</i> -Anisyl cyclohexanecarboxylate	—	<i>p</i> -Methoxy	—	—	275	2000
<i>m</i> -Anisyl cyclohexanecarboxylate	—	<i>m</i> -Methoxy	—	—	273	3000

due to ring B, that is, due to transitions involving excited states of type IV. In agreement with Cilento we ascribe bands to transitions involving either ring A or ring B, although both bands will be influenced by the neighboring ring.



III



IV

From Tables I and III it is seen that substituents in ring A produce changes as might be expected from a consideration of the corresponding benzoic acid spectra. Since the *para*-substituent on account of its *mesomeric* effect will also influence the electron density in the carboxyl group, the change due

to the introduction of the B-ring phenyl group will also be affected. However, in most cases, these additional changes from the benzoic acids to the corresponding phenyl esters are similar and roughly the same as between benzoic acid and phenyl benzoate, that is, a wave-length shift $\Delta\lambda$ of about $3 \text{ m}\mu$ and intensity increase $\Delta\epsilon$ of approximately 4000. The greatest change is observed in the *para*-methoxy compound ($\Delta\lambda_{\max} 12 \text{ m}\mu$, $\Delta\epsilon = 8000$) which may be ascribed to a combination of favorable *mesomeric* and *inductive* effects stabilizing resonance forms of type III. The smallest change occurs in the *para*-nitro compound ($\Delta\lambda_{\max} 1 \text{ m}\mu$), presumably because of the negative *mesomeric* effect of the nitro group.

With a view to investigating the conjugation of the non-bonding *p*-electrons of the oxygen atom and the π -electrons of the B-ring, which Cilento considers to be rather weak, we may consider a number of compounds in which this conjugation might manifest itself. Taking phenyl *p*-anisate as an example where conditions favoring this conjugation already exist, we should expect the introduction of a *para*-nitro group in the B-ring to enhance this effect; the nitro group by withdrawing electrons from the B-ring should stabilize polar excited states of type III. This in fact occurs, and a further bathochromic shift relative to phenyl *p*-anisate accompanied by increased intensity of absorption is observed. Cilento (6) classifies this band separately, but this seems to us to be unnecessary, since we believe it to be due to what is essentially the same type of transition. Introduction of a *para*-nitro group in the B-ring generally would be expected to give rise to a similar effect, and a second example is in fact provided by *p*-nitrophenyl *p*-nitrobenzoate where this change is again observed on comparison with the parent compound, that is phenyl *p*-nitrobenzoate. In these compounds the B-band is not apparent since its maximal absorption closely approximates that of the A-band (see Table III). This was confirmed by determining the maximal absorption of *p*-nitrophenyl cyclohexanecarboxylate, which as expected absorbs maximally in the same region ($\lambda_{\max} 268 \text{ m}\mu$, $\epsilon = 10,000$). Occasionally the ester spectra exhibit the absorption due to the B-ring as maximal absorption, but often this occurs as an inflection. It seems to us unfortunate that Cilento does not record these inflections, that is the submerged maxima, in his table (6), even though the absorption in that region includes some absorption due to the secondary band of ring A.

Reversing the substituents in the above examples has the expected effect. A *para*-methoxy group in the B-ring, because of its *mesomeric* effect, causes a slight hypsochromic shift relative to phenyl benzoate. This is ascribed to the increased electron-availability in the carboxyl group, which enhances the steric effect in that area. The intensity of absorption does not exhibit the expected decrease, since the increased intensity of absorption due to ring B outweighs the supposed decrease accompanying the hypsochromic shift. An analogous effect is observed in *p*-anisyl *p*-anisate relative to phenyl *p*-anisate and in *p*-anisyl *p*-nitrobenzoate relative to phenyl *p*-nitrobenzoate (see Table III). In B-ring *para*-halogen substituted compounds an intermediate effect is observed; the *para*-substituent does bring about a bathochromic shift, which, however, is smaller than that observed for a *para*-nitro substituent in ring B.

(see Table III for the spectra of *p*-chlorophenyl *p*-chlorobenzoate and *p*-iodophenyl *p*-iodobenzoate compared to those of phenyl *p*-chlorobenzoate and phenyl *p*-iodobenzoate respectively). This is readily explained by the intermediate *mesomeric* effects in these compounds.

Meta-methoxy substituents in the B-ring produce a low-intensity band in the 270–280 m μ region. This band is not appreciably influenced by an unsubstituted A-ring as may be seen from the similar B-ring absorption bands in the spectra of *m*-anisyl benzoate and *m*-anisyl cyclohexanecarboxylate. Substituents in the A-ring, however, again give rise to the preferential absorption of the A-ring band (see Table III for the spectra of *m*-anisyl *p*-anisate and *m*-anisyl *p*-nitrobenzoate) which masks the low-intensity absorption due to the B-band.

Finally a number of other B-ring substituted esters are listed in Table III. Sometimes the absorption due to the B-ring is negligible, and the absorption due to the A-ring almost completely predominates as in *p*-chlorophenyl or *p*-iodophenyl benzoates; compounds like *p*-nitrophenyl benzoate, on the other hand, serve as examples where the two bands are of almost the same intensity.

EXPERIMENTAL

The ultraviolet absorption spectra were determined in duplicate by standard methods using a Unicam SP 500 spectrophotometer as described in Part I (8).

Melting points are uncorrected; analyses were carried out in the microanalytical laboratory (Mr. F. H. Oliver) of the Department of Organic Chemistry, Imperial College, London, England, and in the microanalytical laboratory (Mr. A. Bernhardt) of the Max-Planck Institut für Kohlenforschung, Mülheim, Ruhr, Germany.

Benzonic Acids

The commercially available compounds were crystallized to constant melting point and intensity of absorption. *o*-Fluoro-, *m*-fluoro-, *p*-bromo-, and *m*-nitro-benzoic acids were obtained by the oxidation with permanganate of the appropriate toluene according to the method described by Vogel (16). *p*-Bromobenzoic acid had melting point 251–253° (Heilbron and Bunbury (10) give melting point 251–253°). Anal.: Calc. for C₇H₅O₂Br: Br, 39.75%. Found: Br, 40.1%. Light absorptions in ethanol: see Table I.

Phenyl Benzoates

The esters were prepared by standard methods. Solid esters were crystallized from methanol or aqueous methanol to constant melting point and intensity of absorption; liquid esters were distilled to constant refractive index and intensity of absorption.

Phenyl benzoate crystallized as prisms, melting point 70° (Heilbron and Bunbury (10) give melting point 71°); phenyl *p*-chlorobenzoate crystallized as plates, melting point 100° (Birkenbach and Meisenheimer (2) give melting point 100°); phenyl *p*-iodobenzoate crystallized as plates, melting point 133°.

Anal.: Calc. for $C_{13}H_9O_2I$: C, 48.2; H, 2.8; I, 39.15%. Found: C, 47.9; H, 2.6; I, 39.0%. *p*-Chlorophenyl *p*-chlorobenzoate crystallized as plates, melting point 71° (Birkenbach and Meisenheimer (2) give melting point 71°); *p*-iodophenyl *p*-iodobenzoate crystallized as plates, melting point 148°. Anal.: Calc. for $C_{13}H_8O_2I_2$: C, 34.7; H, 1.8; I, 56.4%. Found: C, 34.7; H, 2.1; I, 56.1%. *m*-Anisyl benzoate distilled at 163°, 3 mm., n_D^{27} 1.5751. Anal.: Calc. for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3%. Found: C, 73.9; H, 5.5%. *m*-Anisyl *p*-anisate crystallized as prisms, melting point 102°. Anal.: Calc. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.5%. Found: C, 69.95; H, 5.7%. *m*-Anisyl *p*-nitrobenzoate crystallized as needles, melting point 126°. Anal.: Calc. for $C_{14}H_{11}O_6N$: C, 61.5; H, 4.1; N, 5.1%. Found: C, 61.4; H, 4.3; N, 4.9%. *p*-Chlorophenyl benzoate crystallized as needles, melting point 87° (Autenrieth and Müllinghaus (1) give melting point 86°); *p*-iodophenyl benzoate crystallized as needles, melting point 119° (Willgerodt and Wiegand (17) give melting point 118.5–119.5°).

The light absorption properties of the above-described compounds are recorded in Table III.

Phenyl Cyclohexanecarboxylates

Cyclohexanecarboxylic acid was prepared from cyclohexyl chloride according to the method of Gilman and Zoellner (9) and distilled at 179°, 17 mm.; n_D^{20} 1.4620 as a colorless liquid, which solidified on standing to a solid, melting point 28° (Hiers and Adams (11) give boiling point 105°, 4 mm.; n_D^{38} 1.4520; melting point 29–30°). The esters were prepared in the above-described manner.

Phenyl cyclohexanecarboxylate distilled at 129°, 3 mm.; n_D^{27} 1.5107. Anal.: Calc. for $C_{13}H_{16}O_2$: C, 76.4; H, 7.9%. Found: C, 76.5; H, 8.0%. *p*-Nitrophenyl cyclohexanecarboxylate crystallized as needles, melting point 53.5°. Anal.: Calc. for $C_{13}H_{15}O_4N$: C, 62.6; H, 6.1; N, 5.6%. Found: C, 62.3; H, 5.9; N, 5.7%. *p*-Anisyl cyclohexanecarboxylate crystallized as needles, melting point 64°. Anal.: Calc. for $C_{14}H_{18}O_3$: C, 71.8; H, 7.7%. Found: C, 71.5; H, 7.8%. *m*-Anisyl cyclohexanecarboxylate distilled at 80°, 3 mm.; n_D^{28} 1.5460. Anal.: Calc. for $C_{14}H_{18}O_3$: C, 71.8; H, 7.7%. Found: C, 72.0; H, 7.9%.

The light absorption properties in ethanol of the above-described compounds are recorded in Table III.

ACKNOWLEDGMENTS

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PHOTOLYSIS OF DIETHYL KETONE AT LOW PRESSURES: THE PRESSURE DEPENDENCY OF THE COMBINATION OF ETHYL RADICALS¹

By R. K. BRINTON² AND E. W. R. STEACIE

ABSTRACT

The photolysis of diethyl ketone has been investigated in the pressure range 0.01–30 mm. at 100°, 150°, 200°, and 250° with a variation in absorbed intensity of 1000-fold. Over this wide variation in experimental conditions the kinetics of the reaction show excellent agreement with the mechanism of Kutschke, Wijnen, and Steacie. Under conditions where the production of ethylene by decomposition of the pentanonyl radical was negligible (high light intensity and low ketone pressure), the ratio of the rate of ethylene formed to the rate of butane produced was determined to be 0.12 independent of the temperature. These data indicate that both the disproportionation and combination of ethyl radicals are homogeneous and pressure independent to as low as 0.01 mm. pressure. In addition it is probable that the two reactions are the result of different reaction intermediates as was postulated by Wijnen and Steacie. The abstraction reaction



showed definite heterogeneous character at low pressures similar to the analogous reaction of methyl radicals with acetone studied by Ausloos and Steacie.

INTRODUCTION

The absolute values of the rate constant for the combination of methyl radicals as determined in several independent investigations (2, 5, 10, 11) have differed significantly. Recent papers by Dodd and Steacie (3) and Kis- tiakowsky and Roberts (7) treat this reaction by a pressure dependent mechanism,



in an attempt to reconcile these apparent discrepancies. Both studies were made on the photolysis of acetone at low pressures whereby it is possible to compare the rate of ethane formation by combination to the rate of methane formed by the abstraction mechanism,



The magnitude of the pressure effects on the relative rates of methane and ethane production can be explained for the most part by such a mechanism, but the lower pressure experiments of Dodd and Steacie indicate other anomalies which are strongly surface dependent. These latter effects have been verified by similar low pressure experiments of Ausloos and Steacie (1).

This paper reports on a similar investigation of the pressure dependency of the combination of ethyl radicals formed in the photolysis of diethyl ketone. It was expected that the experimental difficulties would be somewhat greater than in the acetone photolysis since, presumably, the more complex ethyl

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radicals would not show the effect of third body deactivation for the combination reaction at such high pressures as observed for methyl radicals. On the other hand the disproportionation reaction of ethyl radicals into ethylene and ethane seemed to offer a more reliable comparison reaction than the abstraction reaction which most certainly is partly heterogeneous at low pressures in the case of the acetone photolysis.

EXPERIMENTAL

The photolysis apparatus was similar to that of Dodd and Steacie (3). A majority of the experiments were conducted in a cylindrical silica cell of 3.9 cm. diameter and 100 cm. length (volume = 1210 cm.³, surface = 1260 cm.²). Another cell of similar dimensions but having two concentrically mounted inner silica tubes (volume = 1040 cm.³, surface = 3580 cm.²) was used in a series of photolyses at 200° in order to evaluate the effect of increased surface and shorter diffusion distance. The method of temperature control of the cells was identical to that used by the above workers. It was possible to maintain the temperature along the cell's length to $\pm 1^\circ$. No correction was made for that part of the reaction taking place at the cooler end windows since these cold zones represent a rather small fraction of the total reaction volume.

The light which completely filled the reaction cell in all experiments was a well-collimated beam from a B.T.H. ME/D 250 watt high pressure mercury arc operated on a regulated d-c. supply. A Corning 9-53 filter and the long wave length absorption limit of diethyl ketone limited the absorption region to $\lambda\lambda 2800-3200 \text{ \AA}$. A plane aluminized mirror was used at the back cell window to increase the light intensity in some of the photolyses and neutral density filters of chromel deposited on silica plates were used to decrease the intensity in other cases.

The per cent decomposition of diethyl ketone was limited in most of the experiments to 0.5 to 4%. However it was necessary to exceed this amount in those photolyses at pressures less than 0.1 mm. pressure and some decompositions were as much as 20%. In all cases the concentration of diethyl ketone used in the various calculations was the average over the run. A supplementary volume of 15 liters was used in conjunction with the photolysis cell in the photolyses under 1 mm. pressure. This additional gas supply was circulated through the reaction cell at frequent intervals during the photolysis by a mercury diffusion pump. Circulation was not carried out during irradiation since the pumping caused considerable pressure differentials within the cell system. Measurement of diethyl ketone pressure was made by a McLeod gauge.

The analytical vacuum system and the diethyl ketone circulation system employed mercury cutoffs throughout, thus eliminating possible errors due to the absorption of diethyl ketone and reaction products in stopcock grease. Photolysis products were separated by use of a Ward-LeRoy still (9) into three fractions: (a) CO fraction (volatile at -210°), (b) C₂ fraction (volatile at -175°), (c) C₄ fraction (volatile at -115°). These three fractions were analyzed mass spectrometrically. Fraction (a) was essentially pure CO. Analysis showed <0.2% CH₄ to be present. Fraction (b) contained C₂H₆, C₂H₄, and

traces of C_3H_8 , C_3H_6 , and CO_2 . Fraction (c) was predominantly C_4H_{10} with small amounts of butene and propene in experiments carried out at high temperature and low intensity.

Eastman Kodak Company diethyl ketone was dried with anhydrous $CaSO_4$ and fractionated in a 15 plate column. Small portions of the fraction boiling from 100.8° to 101.0° (uncorrected) used as a main supply were thoroughly outgassed before each trial in the vacuum system. The perfluorodimethyl cyclohexane obtained from Halogen Chemicals Inc., Columbia, S.C., was distilled and degassed *in vacuo*.

EXPERIMENTAL RESULTS

In all about 90 runs were made at four different temperatures. The pertinent data for the experiments conducted on diethyl ketone alone are shown in Table I; those shown in Table III refer to the photolyses made in the presence of added perfluorodimethyl cyclohexane, C_8F_{16} .

TABLE I
THE RATES OF PRODUCT FORMATION IN THE PHOTOLYSIS OF DIETHYL KETONE

$[D]$, mole cm. $^{-3} \times 10^7$	R_{CO}	$R_{C_2H_4}^{total}$	$R_{C_2H_6}^{total}$	$R_{C_4H_{10}}$
	mole cm. $^{-3} \text{ sec.}^{-1} \times 10^{13}$			
100°				
0.0320	0.840	0.0875	0.0960	0.715
0.0373	1.26 ^a	0.134	0.140 ^a	1.09 ^a
0.0961	2.47	0.268	0.292	2.12
0.0975	3.92	0.391	0.428	3.38
0.409	2.64	0.272	0.405	2.21
0.468	3.00	0.282	0.475	2.53
0.901	2.92	0.292	0.668	2.26
2.31	4.54	0.428	1.248	3.41
3.69	0.744	0.0519	0.511	0.345
4.29	0.169 ^a	0.0123	0.178 ^a	0.0415
4.29	0.214	0.0122	0.201	0.0520
4.29	0.772	0.0605	0.545	0.328
4.46	0.861	0.0638	0.630	0.368
4.67	1.62 ^a	0.161 ^a	0.986	0.835
4.29	3.48	0.307	1.56 ^a	2.18
4.33	16.2 ^a	1.53 ^a	4.49	11.9 ^a
4.29	63.2	6.25	11.9 ^a	51.5
8.63	4.15	0.202	2.32	1.67 ^a
150°				
0.00345	0.475	0.0468	0.0633	0.385
0.00412	0.587	0.0490	0.0770	0.432
0.00810	1.10 ^a	0.102 ^a	0.129	0.908
0.194	2.85	0.249	0.298	2.40
0.0348	3.64	0.356	0.442	3.13
0.0619	6.08	0.564	0.720	5.27
0.196	7.25	0.684	1.09	6.10
0.353	7.18	0.665	1.41	5.78
0.763	1.06 ^a	0.0876	0.546	0.653
3.78	0.354	0.0130	0.495	0.0352
3.76	1.63 ^a	0.0930	1.67 ^a	0.373
3.76	7.10	0.486	5.05	2.99
3.76	12.0 ^a	0.910	7.21	5.87
3.71	66.1	5.56	22.7	45.1
3.68	199. ^a	17.6	48.9	152. ^a
8.27	6.08	0.292	6.65	1.37 ^a

TABLE I (*Concluded*)
THE RATES OF PRODUCT FORMATION IN THE PHOTOLYSIS OF DIETHYL KETONE

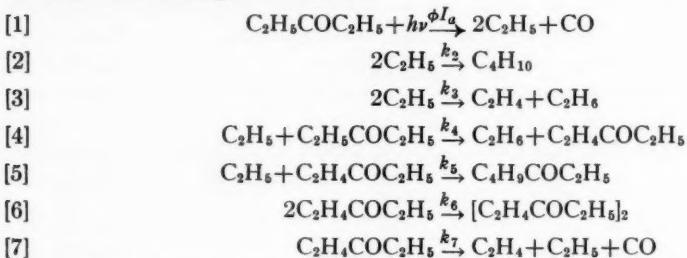
[D], mole cm. ⁻³ × 10 ⁷	R _{CO}	R _{C₂H₄} ^{total}	R _{C₂H₆} ^{total}	R _{C₄H₁₀}
200°				
0.00408	0.703	0.0655	0.0934	0.567
0.00430	0.651	0.0607	0.0955	0.556
0.00425	0.575	0.0645	0.0853	0.478
0.00644	0.813	0.0795	0.116 ^a	0.704
0.00752	0.914	0.0914	0.131 ^a	0.755
0.00792	1.00 ^a	0.103 ^a	0.149 ^a	0.769
0.0170 ^a	1.94 ^a	0.186 ^a	0.268	1.69 ^a
0.0192 ^a	2.12 ^a	0.203	0.306	1.72 ^a
0.0351	4.28	0.418	0.631	3.49
0.165 ^a	8.12	0.766	1.63 ^a	6.53
0.341	6.14	0.553	2.03	4.25
1.56 ^a	2.95	0.189 ^a	2.98	0.707
1.57 ^a	148 ^a	45.5	12.3 ^a	0.107 ^a
1.62 ^a	0.492	0.683	0.0252	0.571
3.24	6.13	6.92	0.336	0.300
5.40	308	157.8	26.2	0.153 ^a
5.52	2.86	4.25	0.139 ^a	0.623
6.84	4.03	6.11	0.143	0.382
8.81	0.513	0.904	0.0244	0.960
9.72	0.942	1.62 ^a	0.0412	1.29 ^a
10.1 ^a	43.0	49.4	2.75	0.366
10.4 ^a	4.71	7.33	0.220	1.04
11.0 ^a	454	311	36.1	0.184
250°				
0.00273	0.638	0.0770	0.133 ^a	0.473
0.00444	1.07 ^a	0.118 ^a	0.212	0.738
0.00720	1.09 ^a	0.123	0.213	0.836
0.00806	1.66 ^a	0.181 ^a	0.307	1.32 ^a
0.169 ^a	2.96	0.316	0.531	2.41
0.0345	5.43	0.615	1.025	4.37
0.0839	9.65	1.03 ^a	2.09	7.19
0.278	27.1	2.70	8.67	18.6 ^a
0.337	6.94	0.828	3.86	3.47
0.708	2.92	0.479	2.82	0.605
1.56 ^a	147. ^a	12.4 ^a	74.5	66.7
1.61 ^a	8.12	0.902	9.33	1.16 ^a
2.85	203	18.4 ^a	144. ^a	86.0
6.43	4.87	0.598	7.70	0.0975
8.68	1.81 ^a	0.377	2.89	0.0240
10.0 ^a	399	32.4	422	87.2
200° "packed cell"				
0.0114 ^a	0.456	0.0499	0.101 ^a	0.402
0.0352	1.60 ^a	0.1675	0.332	1.29 ^a
0.0933	4.17	0.419	0.898	3.43
0.0348	15.6 ^a	1.51 ^a	4.17	12.3 ^a
0.0933	40.1	3.74	14.4 ^a	28.8
2.35	87.2	7.53	40.6	52.5
4.72	154. ^a	11.3 ^a	85.8	82.5

DISCUSSION

The Photolysis Mechanism

Recently a detailed study of the photolysis of diethyl ketone has been made

by Kutschke, Wijnen, and Steacie (8). They explained their results on the basis of the following mechanism—



If the rate of formation of a product, P, is expressed by R_P and the concentration of diethyl ketone by [D] the following expression may be derived.³

$$\log(R_{\text{C}_2\text{H}_6}^{\text{ab}}/R_{\text{C}_4\text{H}_{10}}) = \log(k_4/k_2^{\frac{1}{2}}) + \log([D]/R_{\text{C}_4\text{H}_{10}}^{\frac{1}{2}})$$

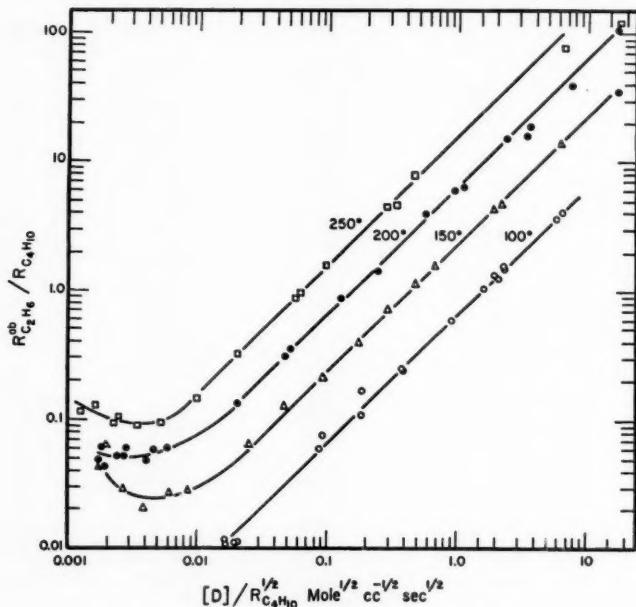


FIG. 1. Plot of $\log R_{\text{C}_2\text{H}_6}^{\text{ab}}/R_{\text{C}_4\text{H}_{10}}$ vs. $\log [D]/R_{\text{C}_4\text{H}_{10}}^{\frac{1}{2}}$.

³ $R_{\text{C}_2\text{H}_6}^{\text{ab}}$ represents the rate of ethane formation by the abstraction reaction [4] to differentiate it from $R_{\text{C}_2\text{H}_6}^{\text{dp}}$, the rate of ethane formed by the disproportionation reaction [3]. This quantity was calculated from the expression $R_{\text{C}_2\text{H}_6}^{\text{ab}} = R_{\text{C}_2\text{H}_6}^{\text{total}} - 0.12 R_{\text{C}_4\text{H}_{10}}$ assuming tacitly that the ratio $k_4/k_2 = 0.12$, independent of experimental conditions. Justification for this procedure is given in the subsequent discussion. $R_{\text{C}_2\text{H}_6}^{\text{ab}}$ is greater than $\Delta R_{\text{C}_2} = R_{\text{C}_2\text{H}_6}^{\text{total}} - R_{\text{C}_2\text{H}_6}^{\text{total}}$, the rate calculated by Kutschke, Wijnen, and Steacie, by the amount of the additional ethylene produced by the decomposition of the pentanoyl radical, $\text{C}_2\text{H}_4\text{COCH}_3$, in reaction [7]. In most cases, however, the difference between $R_{\text{C}_2\text{H}_6}^{\text{ab}}$ and ΔR_{C_2} is small.

The results of the present investigation are shown in Fig. 1 as a plot of $\log R_{C_2H_6}^{ab}/R_{C_4H_{10}}$ vs. $\log [D]/R_{C_4H_{10}}^{\frac{1}{2}}$. Data at the four temperatures cover the pressure range 0.01–30 mm. and represent a variation in absorbed intensity of more than 1000-fold. The series of straight lines of unit slope fit the experimental points well except at the low and high extremes of the variables. Deviations in the low region which occur at pressures under *ca.* 0.4 mm. are treated in detail in a later section; those in the high region are most pronounced at high [D] and low absorbed intensity and are apparent at the two higher temperatures only. A reasonable explanation of these latter anomalies has not been formulated but it is possible that some mode of butane formation in addition to reaction [2] is becoming significant under these conditions. This reaction seemingly must be of the type



where R represents some radical present in the system. Production of detectable amounts of 2-butene and a pentene (2-pentene probably) accompanying the extra amounts of butane could well be the result of the same or a closely related mechanism.

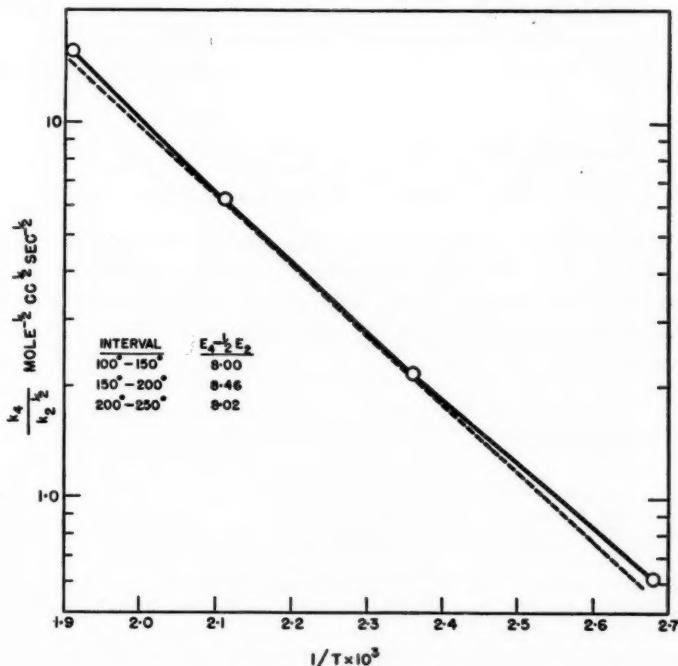


FIG. 2. Arrhenius plot of $k_4/k_2^{\frac{1}{2}}$.

Fig. 2 shows values of $\log k_4/k_2^{\frac{1}{2}}$ calculated from the straight line portions of the curves of Fig. 1 plotted vs. $1/T$. The line connecting the four points shows a

curvature so the values of $E_4 - \frac{1}{2}E_2$ were calculated for each of the three intervals. These activation energies are all higher than the $E_4 - \frac{1}{2}E_2 = 7.4$ kcal./mole reported by Kutschke, Wijnen, and Steacie. Reasons for these differences are not altogether clear but it may be pointed out that almost all of their experiments were conducted at ketone pressures greater than 10 mm. In this region it has been indicated that the values of $k_4/k_2^{\frac{1}{2}}$ tend to be too small at higher temperatures, and hence a calculated activation energy would be low in value. The curvature, although not large, seems to be real and is perhaps the consequence of the diethyl ketone molecules having both a primary and secondary hydrogen atom available for the abstraction process. Activation energies of these two processes would be expected to differ by several kcal./mole (13) and lead to a curvature of the type observed.

No attempt was made in the course of the study to analyze for the products of reactions [5] and [6], ethyl butyl ketone and bipentanonyl respectively. However, it is possible to calculate the rate of production of these two substances by a consideration of the balance of the radicals involved,

$$R_{CO} - R_{C_2H_4}^p = R_{C_4H_{10}} + R_{C_2H_4}^{dp} + R_{C_2H_5COC_4H_9} + R_{(C_2H_4CO)_2} \quad (\text{total radical balance})$$

$$R_{C_2H_6}^{ab} = R_{C_2H_5COC_4H_9} + 2R_{(C_2H_4CO)_2} + R_{C_2H_4}^p \quad (\text{pentanonyl radical balance}).$$

Then

$$\frac{R_{C_2H_5COC_4H_9} [D]}{R_{(C_2H_4CO)_2}^{\frac{1}{2}} R_{C_2H_6}^{ab}} = \frac{k_5}{k_6^{\frac{1}{2}} k_4} \quad \text{and} \quad \frac{R_{C_2H_5COC_4H_9}}{R_{(C_2H_4CO)_2}^{\frac{1}{2}} R_{C_4H_{10}}^{\frac{1}{2}}} = \frac{k_5}{k_6^{\frac{1}{2}} k_2^{\frac{1}{2}}}.$$

Ratios of rates shown in the latter two equations have been calculated for those experiments at the three higher temperatures in which the amount of ethylene formed by reaction [7] was large enough to justify such a procedure. These ratios shown in the second and third columns of Table II have a good

TABLE II
MECHANISM VALIDITY OF THE DIETHYL KETONE PHOTOLYSIS

	$k_5/k_6^{\frac{1}{2}} k_4$ mole $^{-\frac{1}{2}}$ cm. $^{-3}$ sec. $^{-\frac{1}{2}}$	$k_5/k_6^{\frac{1}{2}} k_2^{\frac{1}{2}}$
150° (6 runs)	0.666 ± 0.136	1.50 ± 0.30
200° (10 runs)	0.311 ± 0.061	1.61 ± 0.35
250° (4 runs)	0.135 ± 0.029	1.92 ± 0.35
	$E_4 - E_5 + \frac{1}{2}E_6 = 7.1$ kcal./mole	
	$E_5 - \frac{1}{2}E_6 - \frac{1}{2}E_2 \sim 1$ kcal./mole	

precision at each temperature considering the indirect nature of the calculations involved. In addition $E_4 - E_5 + \frac{1}{2}E_6 = 7.1$ kcal./mole estimated from the second column ratios compares well with $E_4 - \frac{1}{2}E_2 \sim 8.0$ kcal./mole determined directly while $E_5 - \frac{1}{2}E_6 - \frac{1}{2}E_2$ from the third column data is about zero.

Since E_2 , E_5 , and E_6 are activation energies of radical-radical combination reactions and are probably near zero, the agreement of the calculated values with those predicted by analogy to other similar mechanisms is excellent. The above treatment gives strong evidence that only the seven reactions enumerated by Kutschke, Wijnen, and Steacie are required to describe the photolysis of diethyl ketone adequately in the temperature range 150°–250°. The actual magnitude of the derived quantities must be accepted with some reservation because of the type of operations necessary in making the calculations.

The Formation of Ethylene

The ratio $R_{C_2H_4}^{\text{total}}/R_{C_4H_{10}}$ at temperatures under 150° was shown by Kutschke, Wijnen, and Steacie to be about constant at ~ 0.1 . However, at higher temperatures, and especially at high diethyl ketone concentrations and low absorbed intensities, this ratio increased. It was this latter evidence that led them to add reaction [7] to the mechanism of Dorfman and Sheldon (4). In the present study the absorbed intensity and ketone concentration have been varied over a much wider range and the essentials of this study are shown in Fig. 3 where $R_{C_2H_4}^{\text{total}}/R_{C_4H_{10}}$ is plotted vs. R_{CO} .⁴ It is evident that $R_{C_2H_4}^{\text{total}}/R_{C_4H_{10}}$ tends toward a constant value of about 0.11–0.12 as the absorbed intensity is

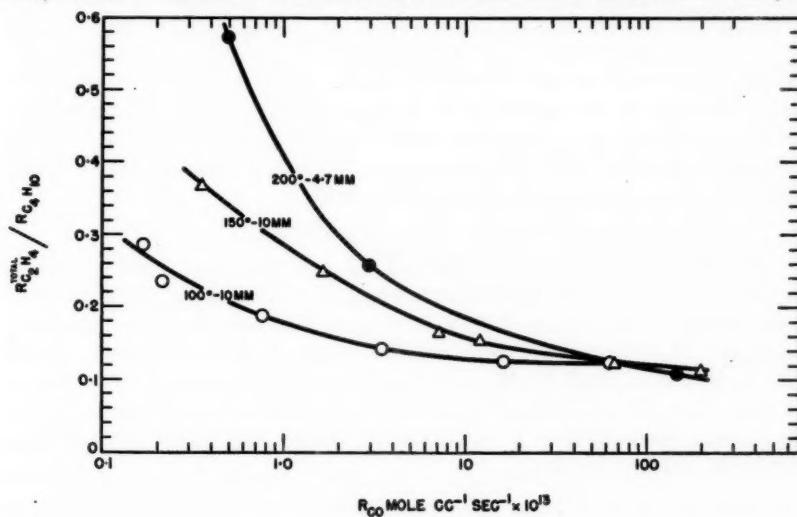


FIG. 3. Plot of $R_{C_2H_4}^{\text{total}}/R_{C_4H_{10}}$ vs. R_{CO} .

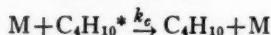
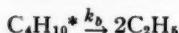
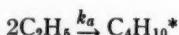
⁴The quantum yield of diethyl ketone was carefully determined by Dorfman and Sheldon (4) at 60° and 120°. They found $\Phi_{CO} = 1.0$ within experimental error and consequently wrote reaction [1] as given previously. Thus it would seem that even at 60° any propionyl radical formed by $C_2H_5COCH_3 \xrightarrow{h\nu} C_2H_5 + C_2H_5CO$ would decompose before appreciable participation in other reactions causing its disappearance. At higher temperatures reactions [4] and [7] constitute a chain mechanism for CO production. However, a calculation from the data of Table I shows that no more than ca. 18% of the total CO is formed by reaction [7] in even the most unfavorable case at 250°. For this reason R_{CO} may be taken as a good approximation of the absorbed intensity.

increased. For a given intensity the deviation from this value is greater at higher temperatures, and, although not indicated in Fig. 3, for fixed temperature and intensity a higher pressure is accompanied by greater deviations. The values of relatively few of the ratios are shown in Fig. 3 but those of all the photolyses follow the generalizations just given in a very regular manner as may be verified by simple calculations from Table I. At 250° the ratio was never lower than about 0.13 even in the very low pressure region. In fact at constant maximum *incident* intensity the minimum of 0.131 was at $[D] = 0.0345 \times 10^{-7}$ mole cm.⁻³; both higher and lower concentrations produced a larger ratio. It is probable that the lower absorbed intensities due to the smaller percentage absorption at the concentrations below $[D] = 0.0345 \times 10^{-7}$ more than offset the effects of the lower concentrations of diethyl ketone tending to decrease the value of $R_{C_2H_4}^{\text{total}}/R_{C_4H_{10}}$. Limits on the intensity imposed by the B.T.H. lamp prevented a real test of this latter explanation.

The evidence given in the preceding sections indicates rather clearly that the disproportionation of ethyl radicals in the photolysis of diethyl ketone in the 3000 Å region is essentially independent of experimental conditions of temperature, intensity, and pressure over a very wide range. The variation in $R_{C_2H_4}^{\text{total}}/R_{C_4H_{10}}$ seems well explained by the production of extra ethylene formed by pentanonyl radical decomposition, reaction [7]. Calculation of $R_{C_2H_4}^{\text{dp}} = 0.12 R_{C_4H_{10}}$ made earlier in the paper is justified on the basis of such a mechanism. The apparent value of the disproportionation to combination for other systems, especially in the photolysis of diethyl mercury, differs markedly from this value. Discussions of these other determinations are given by Ivin, Wijnen, and Steacie (6) and LeRoy and co-workers (12), and it appears that all recent evidence is in agreement with $k_3/k_2 = 0.12-0.15$.

The Combination of Ethyl Radicals. Third Body Effects

The influence of a third body effect on the combination of ethyl radicals in the photolysis process is conveniently demonstrated by comparing the rate of the combination reaction to the rate of some other reaction occurring simultaneously. This comparison reaction must not be dependent on such a third body deactivation. Both Dodd and Steacie (3) and Kistiakowsky and Roberts (7) used the methyl radical abstraction of a hydrogen atom from acetone for this purpose. An analogous treatment in the case of the diethyl ketone photolysis leads to the equations,



$$R_{C_4H_{10}} = \frac{k_a[M]}{k_b/k_c + [M]} [C_2H_5]^2 \quad [M] \gg k_b/k_c, \quad R_{C_4H_{10}} = k_a[C_2H_5]^2;$$

$$[M] \ll k_b/k_c, \quad R_{C_4H_{10}} = \frac{k_a k_c}{k_b} [M][C_2H_5]^2.$$

Thus if $[M]$ is limited to diethyl ketone as a third body, the formation of butane should be independent of $[D]$ above some low pressure. By using the

rate of ethane formation by the abstraction reaction [4], $R_{C_2H_6}^{ab} = k_4[C_2H_5][D]$, as a measure of the ethyl radical concentration, equations [I] and [II],

$$\frac{R_{C_2H_6}^{ab}}{R_{C_4H_{10}}^{\frac{1}{2}}[D]} = \frac{k_4}{k_a^{\frac{1}{2}}} \left[1 + \frac{k_b}{k_c[D]} \right]^{\frac{1}{2}}, \quad [I]$$

$$\frac{R_{C_2H_6}^{ab}}{R_{C_4H_{10}}^{\frac{1}{2}}[D]^{\frac{1}{2}}} = \frac{k_4}{k_a^{\frac{1}{2}}} \left[\frac{k_b}{k_c} + [D] \right]^{\frac{1}{2}}, \quad [II]$$

may be derived. At a single temperature the first of these expressions should approach a constant value with increasing [D] while the latter should tend toward constancy at low [D] values. These two functions are plotted vs. [D] in Figs. 4 and 5. The curves of Fig. 4 follow in a general way the predicted

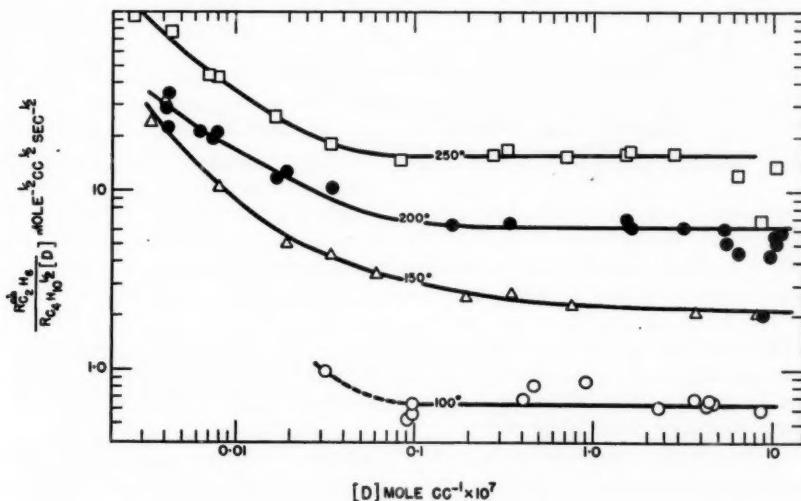


FIG. 4. Plot of $R_{C_2H_6}^{ab}/R_{C_4H_{10}}^{\frac{1}{2}}[D]$ vs. [D].

trend except for the experiments at the highest pressures in which the absorbed intensity was low. A possible explanation of this deviation has been given previously. The curves of Fig. 5 all show a decided increase in the low pressure region where they should be essentially constant if they were to behave as predicted by equation [II]. The dotted curve of Fig. 5 indicates that the data obtained at 200° in the cell with the increased surface area deviate to a still greater extent. It is evident that some heterogeneous reaction is affecting the variables of equations [I] and [II] in the low pressure region. How much of the total defect in the low pressure values of equation [I] from the high pressure value of $R_{C_2H_6}^{ab}/R_{C_4H_{10}}^{\frac{1}{2}}[D]$ is due to surface effects and how much is due to a third body deactivation anomaly is difficult to assess by this treatment. It seems significant that the minima in the curves of Fig. 5 occur at lower pressures (*ca.* 0.1 mm.) than do the corresponding ones (0.5–2 mm.) for the photo-

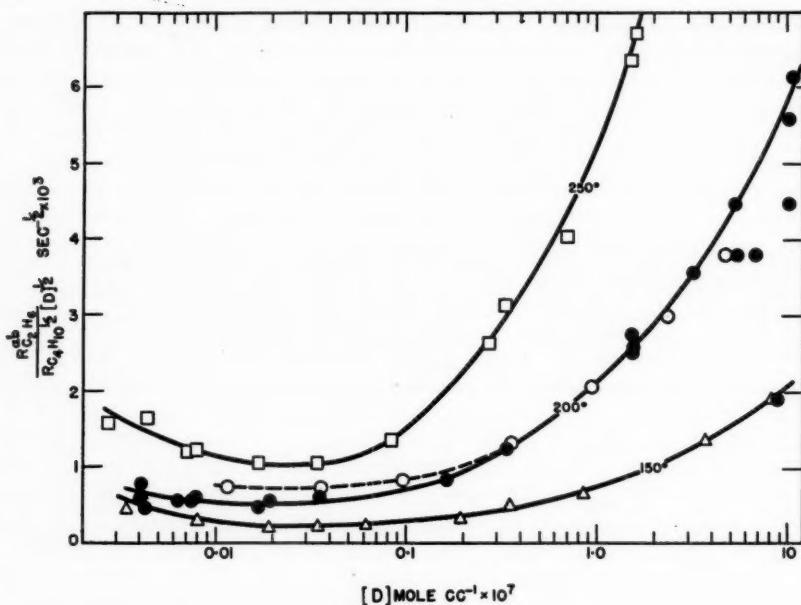


FIG. 5. Plot of $R_{C_2H_6}^{ab}/R_{C_4H_{10}}^{1/2}[D]^{1/2}$ vs. $[D]$.

lysis of acetone given by Ausloos and Steacie (1). Since the influence of a heterogeneous reaction should not be appreciably different for the two ketones, the minima at lower pressures in the case of diethyl ketone could well indicate a much smaller third body effect.

A less complex and seemingly more meaningful treatment of the third body effect in the case of diethyl ketone is to compare the rate of disproportionation to the rate of combination. Although the reactants are identical in the two reactions it will be assumed that the two reaction intermediates differ and that the complex for the disproportionation reaction is not influenced by a third body effect. The disproportionation scheme will be

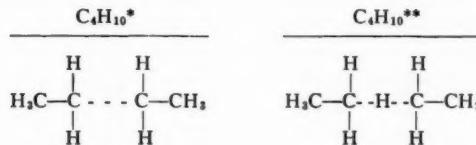


If this latter rate is combined with the expression already derived for the third body mechanism for butane formation, the rate of disproportionation to combination becomes

$$\frac{R_{C_2H_4}^{dp}}{R_{C_4H_{10}}} = \frac{k_\alpha k_\gamma / (k_\beta + k_\gamma)}{k_\alpha k_c [D] / (k_\beta + k_c [D])}.$$

Since it has been found that this ratio is 0.12 independent of experimental conditions, it must be true that $[M]k_c \gg k_b$ or that the combination reaction is not showing a dependency on a third body deactivation down to pressures as low as 0.01 mm.

It is necessary to substantiate the two postulates made in the previous discussion: (a) the reaction intermediates of the disproportionation and combination reactions differ, and (b) the disproportionation complex will not be third body dependent. The two complexes may be represented as



These same complexes were postulated by Wijnen and Steacie (14) to explain the composition of the various deuterated ethylenes formed in the photolysis of 2,2'4,4' tetradecaethoxydiethyl ketone. Their evidence strongly supports a "head to head" intermediate for the combination and a "head to toe" intermediate for the disproportionation.

A consideration of the possible fates of the two complexes and the energetics involved leads to the conclusion that they should have very different response to a collisional deactivation. The combination of two ethyl radicals to form $C_4H_{10}^*$ produces a molecule essentially of the butane configuration which is "hot" by about 80 kcal./mole compared to the final butane product. If the possibilities of H atom rearrangements are ruled out as seems to be the case from Wijnen and Steacie's results (14), the only possible reactions available for $C_4H_{10}^*$ are deactivation by collision and dissociation into the original ethyl radicals. The $C_4H_{10}^{**}$ complex, on the other hand, cannot be deactivated to a stable molecule without an H atom shift. In addition the complex is not as "hot" as is $C_4H_{10}^*$ when it is compared to its end products, C_2H_4 and C_2H_6 ($2C_2H_5 \rightarrow C_2H_4 + C_2H_6, \Delta H = -59$ kcal./mole). Most important, however, is the ability of the two product fragments of almost equal mass to distribute this excess energy between them so that the 30 kcal./mole carried by each product is far below that necessary to decompose either the ethylene or ethane.

A further test of the role of a third body was attempted by adding perfluorodimethyl cyclohexane to the reaction system. This gas was chosen because (a) its physical characteristics allowed an easy separation from the products of the photolysis, (b) it was transparent to the radiation used in the photolysis, (c) it was inert to the various radicals formed in the photolysis, and (d) the data of Dodd and Steacie indicated that its efficiency as a third body was quite high. Runs were made at 200° and 250° using essentially constant intensity and ketone concentration but with varying amounts of C_8F_{16} added. Experimental data and various calculated parameters for these runs are given in Table III. The most significant and unexpected result of the experiments was the increase in $R_{C_2H_4}^{\text{total}}/R_{C_4H_{10}}$ with an increase in C_8F_{16} concentration. Inas-

TABLE III
THE EFFECT OF ADDED PERFLUORODIMETHYL CYCLOHEXANE, C_8F_{16}

[D] (mm.)	C_8F_{16} (mm.)	R_{CO}	$R_{C_2H_4}^{\text{total}}$ mole cm. ⁻³ sec. ⁻¹ $\times 10^{13}$	$R_{C_2H_6}^{\text{ab}}$	$R_{C_2H_4}^{\text{total}}$ $R_{C_4H_{10}}$	$R_{C_2H_6}^{\text{ab}}$ $R_{C_4H_{10}}^{\frac{1}{2}} [D]$
200°						
0.0234	0	1.00	0.103 ^a	0.769	.0535	0.134
0.0234	0.552	0.958	0.106 ^a	0.783	.0404	0.136
0.0215	1.60	0.933	0.107 ^a	0.746	.0367	0.144
0.0235	4.95	0.971	0.127 ^a	0.710	.0389	0.180
250°						
0.0236	0	1.09 ^a	0.123	0.836	.108	0.147
0.0246	0.177 ^a	1.18 ^a	0.127	0.874	.107	0.145
0.0248	1.16 ^a	1.19 ^a	0.162	0.794	.149	0.204
0.0238	4.99	1.19 ^a	0.169	0.767	.120	0.220

much as the formation of butane would not be expected to be made less favorable by an added gas, the increase in the ratio must be attributed to an enhanced C_2H_4 formation. It seems likely that the unimolecular pentanonyl radical decomposition, reaction [7], is in its pressure dependent region at 0.02 mm. of diethyl ketone. Addition of C_8F_{16} must aid in the deactivation of the pentanonyl reaction complex thus increasing the C_2H_4 formation.

Values of $R_{C_2H_6}^{\text{ab}}/R_{C_4H_{10}}^{\frac{1}{2}}[D]$ in the last column of Table III, although not constant to a high degree of precision, show no trend with increasing C_8F_{16} concentration. The poorer agreement between the values is compatible with the difficulty of analyzing for the photolysis products contained in the very large amounts of added C_8F_{16} . The lack of any appreciable effect of even high C_8F_{16} concentrations on $R_{C_2H_6}^{\text{ab}}/R_{C_4H_{10}}^{\frac{1}{2}}[D]$ may substantiate the independence of the ethyl radical combination to pressure. Unfortunately this latter evidence is complicated by the unevaluated effect of the added gas on the heterogeneous formation of ethane. It might be expected that the greater gas concentration would reduce the rate of radical diffusion to the wall and in addition perhaps reduce the concentration of adsorbed substrate. Since both these effects would tend to decrease the heterogeneous ethane formation it is surprising that the values in the last column of Table III do not decrease at the high C_8F_{16} concentrations.

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NOTE

A FURTHER OBSERVATION ON THE BIOGENESIS OF HYOSCYAMINE¹

BY LÉO MARION AND ALAN F. THOMAS²

It has been shown previously that in mature *Datura stramonium* plants putrescine is not involved in the formation of either hyoscine or hyoscyamine (3), and that ornithine is a precursor of hyoscyamine but not of hyoscine (7, 8). This fact has been interpreted as implying a different mode of formation for the two alkaloids (8), although the conclusion that hyoscine is no longer synthesized in the mature plant, while hyoscyamine is, is equally plausible (cf. 12).

In all cases of nitrogen methylation in plants studied so far methionine has always been found to act as a precursor of the methyl groups (1, 2, 4, 9) although formate and choline did not always perform that role (4, 9). Therefore, it appeared legitimate to assume that in *D. stramonium* methionine would perform the same function. On feeding C¹⁴-methyl-labelled methionine to mature *D. stramonium*, both hyoscyamine and hyoscine should be radioactive because of the presence of an N—C¹⁴H₃ group in each, if both alkaloids were still being synthesized, albeit by different pathways. On the other hand, were hyoscine no longer synthesized at the time of the experiment, then only the hyoscyamine should be radioactive.

It has now been found that when C¹⁴-methyl-labelled methionine was fed to the mature plant and the alkaloids isolated, only the hyoscyamine but not the hyoscine was radioactive. There seems to be little doubt, therefore, that as stated by Trautner (12) hyoscine is formed at a comparatively early stage in the development of the plant, after which hyoscyamine is formed exclusively. Although it is possible that hyoscine could be synthesized from a different precursor, the fact that this base is no longer produced in the mature plant accounts for the failure of ornithine-2-C¹⁴ to give rise at this stage to radioactive hyoscine (7, 8).

Very recently, in a study of the metabolism of glycine-2-C¹⁴ in vigorously growing *D. ferox*, Evans and Partridge (6) found that both hyoscine and meteloidine were radioactive, but also they observed that the labelling of the alkaloids varied significantly with the state of maturity of the plant.

In reporting the results of previous experiments on feeding ornithine-2-C¹⁴ to *D. stramonium*, the radioactivity of the amino acid fraction obtained from the plant extract was assumed to be due to the presence of excess labelled ornithine (8). Examination of this fraction has now revealed that it contained practically no ornithine, and hence the radioactivity of this fraction must be attributed to other amino acids arising from the metabolism of ornithine.

EXPERIMENTAL

dl-C¹⁴-Methionine prepared from *dl*-homocysteine according to the method of Melville, Rachele, and Keller (10) had an activity of 1.07×10^7 counts per

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min. per mgm. (1.59×10^9 counts per min. per millimole); and 74 mgm. was fed to a mature *D. stramonium* plant as described previously (3). The methionine was rapidly taken up by the plant, over 90% having been absorbed in four days at which time it was harvested. The radioactivity then was distributed as follows in counts per min. per mgm. (before drying): roots, 1000; leaves, 9; seeds, 4. The whole plant was dried at 100° in an oven for 48 hr., and the crude alkaloids isolated as described already (8). To the crude mixture of alkaloids 250 mgm. each of hyoscine and hyoscyamine was added and the mixture was dissolved in ether. The total activity of the crude solution at this stage was 6.34×10^6 counts per min. (i.e. ca. 1% of the total activity administered). Separation of the alkaloids was effected by chromatography on a kieselguhr column as described by Evans and Partridge (5) since the method previously used (8, 11) was found to be unreliable. The alkaloids were purified finally by recrystallization of the aurichlorides to constant activity. Hyoscyamine was found to have an activity of 5.8×10^4 counts per min. per millimole, while that of hyoscine, although faintly positive at first, had dropped to zero after three recrystallizations from water.

The N-methyl group was eliminated from the hyoscyamine in a Herziger-Meyer determination, the reaction being carried out as described by Dubeck and Kirkwood (4) up to the precipitation of the tetramethylammonium reineckeate. The precipitate was dissolved in acetone and chromatographed on alumina which retained the impurities while the tetramethylammonium reineckeate passed through the column. The solution was concentrated under reduced pressure at room temperature and diluted with water. The salt crystallized as pale pink leaflets, m.p. $288\text{--}289^\circ$ (decomp.). Its activity was 5.4×10^4 counts per min. per millimole.

As reported previously (8), *D. stramonium* fed with C¹⁴-labelled ornithine yielded when extracted, besides labelled hyoscyamine, a radioactive amino acid fraction. This fraction has now been examined further by two-dimensional paper chromatography. It was found to contain mainly the following free amino acids: asparagine, glycine, alanine, proline (trace), methionine, and aspartic acid. Neither ornithine nor glutamic acid was present in appreciable concentration.

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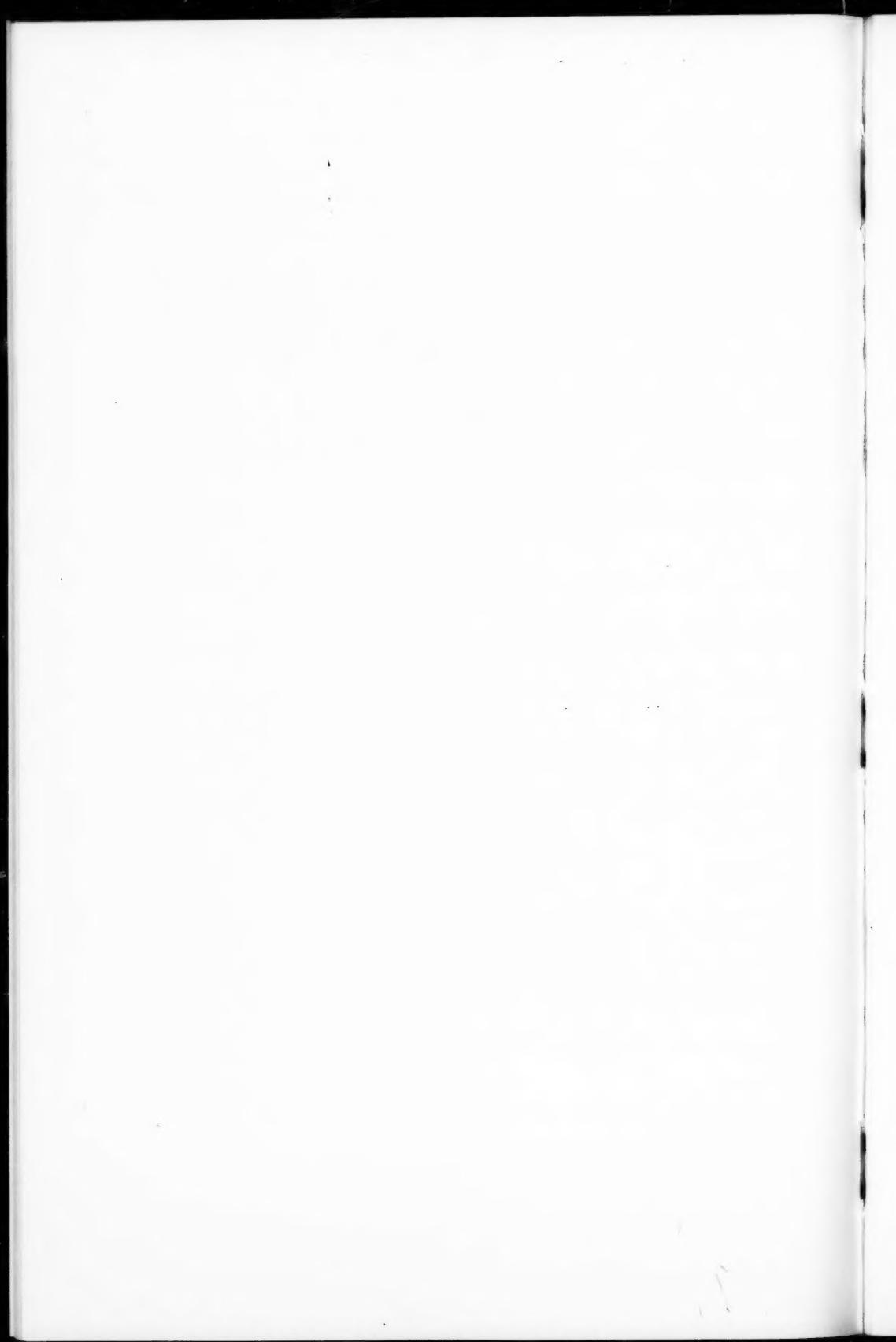
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ADDITIONS AND CORRECTIONS

Page 1450. In line 18, between the words "a axis" and "which" insert: ".Trial and error methods eventually led to a reasonable trial structure looking down the a axis".

Page 1489. In Reference 8, 1491 should read 1625.





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